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Discovery of cloud top ozone on Venus

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Abstract

After the first sporadic detections of an ozone (O_3) nighttime layer in the 90-100 km altitude range (Montmessin *et al.*, 2011), we report here the discovery of another, permanent ozone layer on Venus, restricted to high latitudes (polewards of 50° both N and S) and located at the upper cloud level near 70 km. This detection was performed during a reanalysis of the whole SPICAV-UV nadir dataset through UV absorption near 250 nm in the backscattered solar light. The O_3 volume mixing ratio peaks in the 10 to 20 ppbv range, yielding observable column densities in the 0.1 to 0.5 Dobson units (DU), comparable to nominal values on Mars but much smaller than for Earth (~ 300 DU). These measurements are supported by our 3D-photochemical model coupled with the LMD-IPSL GCM (Lebonnois *et al.*, 2010), which indicates that the ozone layer identified by SPICAV results from downward transport of O_2 (~ 50 ppmv) molecules over the poles by the mean meridional circulation. Our findings do not contradict previous upper limits (< 2 ppmv) based on O_2 measurements (Mills, 1999), since they were

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restricted to lower latitudes only.

Keywords:

Venus, atmosphere, Ultraviolet, observations, Atmospheres, composition

1 **1. Introduction**

2 Ozone (O₃) has been observed in the ultraviolet (UV) domain in all three
3 telluric atmospheres of the inner solar system: on Earth, discovered in the
4 early 20th century; on Mars, by Barth *et al.* (1973) in the early 1970s from
5 *Mariner 9*; and more recently on Venus using the SPICAV-UV spectrome-
6 ter on board *Venus Express* in stellar occultation mode (Montmessin *et al.*,
7 2011). Unlike Earth and Mars, this Venusian ozone layer appears to be spo-
8 radic and located at very high altitudes (circa 10⁻² mbar for Venus instead
9 of 1-50 mbar for Earth and Mars), so that it is the thinnest of all in terms of
10 local number densities. Here we report the discovery of permanent, denser
11 ozone polar caps located at high latitudes near cloud top level, where pressure
12 is similar to ozone-bearing layers in the atmospheres of Mars and Earth.

13 This discovery happened during our reanalysis of the whole SPICAV-
14 UV nadir dataset after the end of *Venus Express* in 2014. Although 1D
15 photochemical models did not predict any significant O₃ near cloud top (Yung
16 and Demore, 1982; Krasnopolsky, 2013), we observed in our first processing of
17 SPICAV-UV nadir data (Marcq *et al.*, 2011, Fig. 12) that another absorption
18 occurred sometimes near 250 nm, and suggested that it might be caused by
19 ozone.

20 Aside from the primary goal of our reanalysis (namely, investigating the
21 climatology of cloud top SO₂ in the 2006-2014 timeframe) that will be dis-

22 cussed in subsequent papers, we included a possible ozone absorption in
23 our study and found numerous robust detections at high latitudes that are
24 detailed hereafter. The observational data set and the pre-processing into
25 spectral radiance factors are described in Sec. 2, our forward radiative model
26 is detailed in Sec. 3, and our results are discussed, compared with previous
27 upper limits, and interpreted using a 3D photochemical model in Sec. 4.

28 **2. Observations**

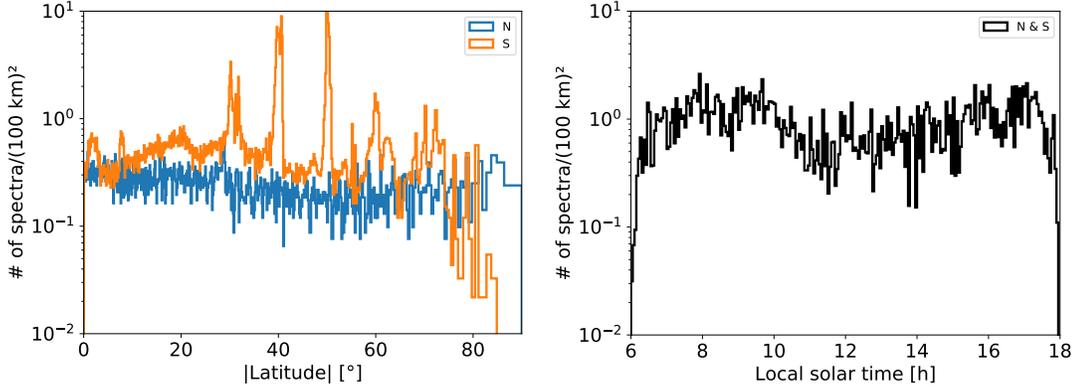
29 *2.1. Overview*

30 The SPICAV-UV spectrometer (Bertaux *et al.*, 2007) on board *Venus*
31 *Express* covered the 118-320 nm spectral range, sampled at 0.55 nm with a
32 Field of View $1^\circ \times 3.16^\circ$. Our studies have used 5 lines of the CCD (from
33 line #141 to #145) corresponding to the region where the spectrometer slit is
34 narrow and the spectral resolution higher (1 nm). Integration time was 0.64 s.
35 Although SPICAV-UV can be used also in limb or occultation modes, we only
36 focus here on day side near nadir observations (whenever the line of sight
37 intersects the solid planet), therefore observing the sunlight backscattered
38 by the upper clouds of Venus.

39 *2.1.1. Coverage*

40 The spatial coverage of these 1508 near nadir observations acquired be-
41 tween orbits #0041 (2006-06-01) and #3146 (2014-11-20) is shown on Fig. 1.
42 We can see that very few observations were acquired southwards of 80°S
43 compared to northwards of 80°N . This is due to the quasi-polar and highly
44 elliptical orbit of *Venus Express* (pericenter near 78°N). Also, the coverage in

Figure 1: *Left*: areal coverage of near nadir SPICAV-UV observations with respect to latitude for north and south hemispheres. *Right*: areal coverage of near nadir SPICAV-UV observations with respect to local solar time for both hemispheres.



45 the southern hemisphere is less uniform than in the northern one, since most
 46 southern observations were done in *pointing* mode, where SPICAV FOV was
 47 fixed relative to the Venusian surface. In contrast, most northern observa-
 48 tions were done in *latitudinal scan* mode, sweeping a large latitudinal swath
 49 under the spacecraft orbit with a constant (and small) emission angle. Cov-
 50 erage in local time is more regular, with a small decrease near local noon
 51 due to spacecraft constraints on the phase angle (direct illumination of the
 52 spacecraft radiator was limited to short amounts of time).

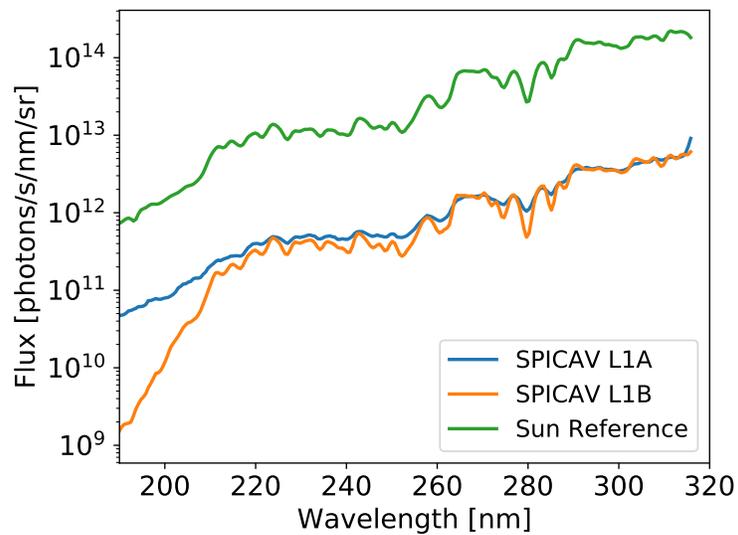
53 2.2. Instrumental correction

54 The first steps of the processing have changed little compared to those
 55 described in Marcq *et al.* (2011). First, non-uniform dark current templates
 56 (acquired with light intensifier switched off) are rescaled in order to match the

57 operational parameters (notably, the temperature) at the time of the science
58 mode operation. These dark frames are subtracted from the light-exposed
59 frames. Cosmic hits are removed, as well as a pseudo-periodic electronic
60 readout artifact. Flat-field corrections are also implemented. Based on the
61 rich spectral structure of the solar spectrum in the 200-315 nm range as can
62 be seen in Marcq *et al.* (2011, their Fig. 1), sub-pixel wavelength assignment
63 could be performed for each acquisition (there is a typical drift of 1-2 pixels
64 (0.54-1.08 nm) during a 30 min long observation sequence).

65 External solar stray light is not a problem for near-nadir observations,
66 since the phase angle is always smaller than 90° so that Venus backscatter-
67 ing is always dominant. Internally, one significant source of contamination
68 comes from the blurring due to the point spread function (PSF) of the in-
69 strument. Its shape is empirically modeled as a two dimensional Gaussian
70 core with a radius of a few pixels, summed to an extended halo, which de-
71 crease asymptotically as a power function. The parameters of this model
72 have been preliminary estimated by exploiting a few technical observations.
73 In order to reduce the far wing impact of the PSF and tentatively access the
74 native spectral resolution of the instrument, an inversion is performed using
75 an iterative accelerated damped Richardson-Lucy algorithm (White, 1994;
76 Biggs and Andrews, 1997). This step greatly reduces spectral distortions
77 due to spectral blur (Fig. 2). Also, it accounts for and subtracts the cross-
78 contamination of spatially separated CCD lines. This happens for instance
79 when faint spectra are acquired in the narrow segment of the slit while the
80 wide segment is fully illuminated.

Figure 2: *Left*: Observed spectrum before (L1A) and after (L1B) Richardson-Lucy deconvolution, compared to our reference solar spectrum at SPICAV resolution. Note that the deconvolution (i) restores the full instrumental resolution of the solar features; and (ii) effectively removes contamination due to the extended halo of the PSF at shorter wavelengths.



81 *2.3. Spectral radiance calibration*

82 In order to get an absolute photometric calibration for the spectral ra-
83 diance $B(\lambda)$, we have preliminarily observed a few selected UV-bright stars,
84 for which a reference spectra existed in the CALSPEC database (Bohlin
85 *et al.*, 2014). From these observations, an effective area can be defined for
86 each wavelength as the ratio between the number of detected photons per
87 unit of time and the incoming stellar flux. This effective area is of course a
88 function of the wavelength, but also a function of the age of the instrument.
89 The actual calibration step consists in multiplying the nadir spectra by a
90 calibration vector which takes into account the amplifier gain, the effective
91 area and the angular field of view of each pixel. These studies suggest that
92 for the low gain values used in these near-nadir observations, no significant
93 aging trend should be expected over the duration of the mission.

94 *2.4. Radiance factor calibration*

95 Following our previous work (Marcq *et al.*, 2011, 2013), we define the
96 *radiance factor* $\beta(\lambda)$ through the expression $\beta(\lambda) = \frac{I(\lambda) \times \pi \text{ sr}}{F_{\odot}(\lambda)}$ where $I(\lambda)$ is
97 the received spectral intensity and $F_{\odot}(\lambda)$ is a reference top-of-atmosphere
98 solar spectral irradiance as received by Venus. $\beta(\lambda)$ differs from the spectral
99 albedo by not depending on the solar zenith angle value, and thus can be
100 meaningfully defined even on the night side near the terminator – solar zenith
101 angle (SZA) a few degrees larger than 90° , where some scattered solar light
102 can be still detected. Although our pseudo-spherical radiative forward model
103 can account for such a geometry, we restrict our analysis to $\text{SZA} < 88^{\circ}$, so
104 that we can still consider the Sun as a point-like source (i.e. considering
105 the same airmass over the whole extent of the solar disk). Since the angular

106 diameter of the Sun as seen from Venus is a mere 0.8° , this approximation
107 results in a relative error smaller than 0.5% on our synthetic radiance factors,
108 according to our numerical testings.

109 For the scope of this work, our reference spectra are the 30 days running
110 averages of the daily solar irradiance from the SOLSTICE II database (Mc-
111 Clintock *et al.*, 2005). The actual data in the MUV range have been slightly
112 corrected in order to fall back to a previous calibration, as the more recent
113 one has a feature around 230-240 nm for which no good agreement can be
114 found in the models, whichever the set of chosen parameters.

115 The ratio between observed spectral radiances and the solar spectral irra-
116 diance is very sensitive to precise spectral alignment and matching spectral
117 resolution, due to the numerous solar lines. This results in “wiggles” on a
118 wavelength scale of the apparent line width (1-2 nm). It is reasonable to as-
119 sume that the expected radiance factor is smooth on this scale. We therefore
120 applied a regularizing procedure consisting in: (a) determining the relative
121 alignment of the spectra at the level of 0.05 nm; (b) locally adjusting the
122 spectral resolution for each line; (c) performing a sensitivity analysis and
123 retaining only a few dozen wavelength positions (typically the two inflec-
124 tion points for each of the solar spectral lines) with vanishing dependence on
125 the resolution parameter; (d) interpolating between the fixed points with a
126 smooth function.

127 **3. Forward Model**

128 The core of our forward model is the publicly available SPSSDISORT v2.0
129 generic radiative transfer code. SPSSDISORT is the pseudo-spherical ver-

130 sion of the well-known DISORT code (Stamnes *et al.*, 1988; Dahlback and
131 Stamnes, 1991).

132 3.1. Vertical profiles

133 Our model atmosphere is divided into 30, 2-km thick homogeneous layers
134 extending from $z = 50$ km ($P = 1037$ mbar) up to 110 km. The albedo of
135 the virtual surface at the bottom of our model is set to 0.33, but we checked
136 that the model does not exhibit any sensitivity to this bottom albedo, since
137 the overlying atmosphere is optically thick (and absorbing) at all considered
138 wavelengths.

139 3.1.1. Clouds & hazes profiles

140 We consider a simplified version of the bimodal distribution derived by Lug-
141 inin *et al.* (2016). Size distributions and optical properties of both modes are
142 detailed hereafter (§3.3).

143 Particle number density (in units of particles $\cdot\text{m}^{-3}$) for mode 2 is given
144 by: $n_2(z) = 10^8$ for $z < Z_2$ and $n_2(z) = 10^8 \times \exp\left(\frac{Z_2 - z}{4.5 \text{ km}}\right)$ for $z > Z_2$. The
145 control altitude Z_2 is a fitted parameter. It is related, but should not be
146 confused with the $Z(\tau_\lambda = 1)$ altitude which classically defines the cloud top
147 altitude (nadir optical depth equal to 1) – e.g. at $\lambda = 250$ nm, we have
148 $Z(\tau = 1) = Z_2 + 4.95$ km.

149 Particle number density for mode 1 is tied to mode 2 number density
150 profile according to: $n_1(z) = \min[2 \times 10^8; 500 \times n_2(z)]$.

151 3.1.2. Gaseous species profiles

152 The number densities of gas molecules $n_0(z)$ in each layer is computed
153 according to hydrostatic equilibrium, taking into account the decrease of

154 gravity with increasing altitude (the acceleration of gravity at the bottom
 155 of the model being set to 8.725 m/s^2). The temperature profile is taken
 156 from VIRI-2 (Moroz and Zasova, 1997), and the molecular mass vertically
 157 uniform at 43.4 g/mol . CO_2 and N_2 volume mixing ratios are also vertically
 158 uniform – the part of the atmosphere that we model lies entirely within
 159 the homosphere – and respectively equal to 96.5% and 3.5% . Adopting a
 160 fixed temperature profile is a reasonable approximation, since it has far less
 161 consequences for modeling Venus UV reflectivity than for thermal infrared
 162 sounding. SO_2 mixing vertical profile is parameterized as follows: $f(z) =$
 163 $\min [150 \text{ ppmv}; f_{70 \text{ km}} \times \exp(\frac{70 \text{ km} - z}{3 \text{ km}})]$. SO_2 mixing ratio at 70 km , $f_{70 \text{ km}}$, is
 164 the fitted quantity for SO_2 .

165 SO vertical profile follows a simplified parameterization from Krasnopol-
 166 sky (2018): it is tied to 10% of SO_2 profile from the top of our model down-
 167 wards, following the same scale height as SO_2 (namely 3 km), reaching a
 168 maximum in the lower atmosphere at 1 ppmv , and dropping to 0 below
 169 this maximum. Based on our numerical modeling with the Venus LMD-
 170 IPSL-GCM (see §4.2), O_3 mixing ratio profile is considered uniform in the
 171 $55\text{-}70 \text{ km}$ range, and null out of this range. Its mixing ratio in the $55\text{-}70 \text{ km}$
 172 range is a fitted parameter, but we should keep in mind that retrieved O_3
 173 VMR is strongly dependent on our assumed vertical profile. OCS absorption
 174 was shown by Haus *et al.* (2015) to be noticeable near 240 nm , so we included
 175 (but did not fit) a fixed OCS vertical profile according to the above refer-
 176 ence (Haus *et al.*, 2015): $f_{\text{OCS}}(z) = \min [42.5 \text{ ppbv}; 10^{-7} \times \exp(\frac{50 \text{ km} - z}{14.427 \text{ km}})]$.

177 3.2. Gaseous cross-sections

178 Absorption cross-sections of CO₂, O₃, OCS, SO₂ and SO are taken from
179 various sources. For CO₂, whose cross-sections were extracted from Parkin-
180 son (2003), we interpolated between 195 and 295 K assuming that $\log \sigma_{\text{abs}}$
181 is a linear function of $1/T$. We used the same temperature interpolation for
182 SO₂ cross-sections and used the same primary sources, spectral ranges and
183 temperature range as Jessup *et al.* (2015), namely: (a) Rufus *et al.* (2003) at
184 295 K and 198 K, above 200 nm; (b) Freeman *et al.* (1984) at 213 K below
185 240 nm; (c) Wu *et al.* (2000) at 295 K above 240 nm.

186 Recent SO cross-section measurements are rare in the databases; we used
187 data from Phillips (1981) in the 190-230 nm range provided by Frank Mills
188 (priv. comm.), and extrapolated the cross-section for shorter wavelengths
189 with a best-fitting parabola: $\log_{10}(\sigma_{\text{abs}}/\text{cm}^2) = -\left(\frac{\lambda-200.132 \text{ nm}}{20.961 \text{ nm}}\right)^2 - 16.780$.
190 For wavelengths longer than 230 nm, SO cross-section is taken constant at
191 $3 \times 10^{-20} \text{ cm}^2$.

192 O₃ cross-section is taken from Sander *et al.* (2011) for a temperature of
193 218 K in the 196-343 nm range. OCS cross-section is also taken from Sander
194 *et al.* (2011) for a temperature of 225 K in the 186-292 nm range.

195 CO₂, SO₂ and SO absorption cross-sections feature a line-resolving, high
196 spectral resolution (around 0.2 nm). Our forward model is however used here
197 at a coarser spectral resolution (since SPICAV-UV FWHM is around 1 nm)
198 through the convolution within a Gaussian window of the computed high-
199 resolution transmission in each computational layer, which is then converted
200 to a low-resolution optical depth: $\tau = -\ln[\langle T \rangle]$ where T is the transmission
201 and $\langle \rangle$ stands for the running average of the spectral transmission over the

202 chosen spectral resolution. Rayleigh scattering cross sections for CO₂ and
203 N₂ are taken from Snee and Ubachs (2005).

204 3.3. Mie theory calculations

205 The radiative transfer model requires the scattering properties of both
206 mode 1 and mode 2 that make up the clouds and haze of Venus. These prop-
207 erties are: their single scattering albedo $\varpi_0(\lambda)$, the extinction cross-section
208 $\sigma_{\text{ext}}(\lambda)$, the coefficients of the Legendre expansion of their phase functions
209 $p_i(\lambda)$. They are computed using the standard BHMIE Fortran implementation
210 of the Bohren and Huffman (1983) code for 17 discrete wavelengths from 170
211 to 320 nm every 10 nm. A bimodal particle distribution is considered, assum-
212 ing a log-normal distribution following Luginin *et al.* (2016): $r_{\text{eff}} = 0.12 \mu\text{m}$,
213 $\nu_{\text{eff}} = 0.15$ for mode 1; $r_{\text{eff}} = 0.8 \mu\text{m}$, $\nu_{\text{eff}} = 0.15$ for mode 2. The real
214 part of the refractive index follows $m_r(\lambda) = 1.526 - 3.05 \times 10^{-4} (\lambda - 200 \text{ nm})$
215 according to Hummel *et al.* (1988) for a 75% – 25% H₂SO₄-H₂O mixture.
216 The imaginary part of the refractive index is assumed to be $m_i(\lambda) = 10^{-3}$
217 for mode 2 particles, and $m_i(\lambda) = m_i(250 \text{ nm}) \times \exp\left(\frac{\lambda - 250 \text{ nm}}{50 \text{ nm}}\right)$ for mode 1
218 particles. $m_i(250 \text{ nm})$ is an adjustable parameter representative of the un-
219 known UV absorber concentration in mode 1 droplets. Both these choices
220 for m_i allow our retrievals for cloud top altitudes and m_i to be consistent
221 with commonly accepted values (Ignatiev *et al.*, 2009; Titov, 2017), as well
222 as minimizing spurious correlations of our cloud parameters with airmass
223 and/or solar zenith angle. Please note that SO₂ and O₃ retrievals, which
224 exhibit a specific spectral dependency (absorption bands), do not suffer from
225 this degeneracy. Look-up tables of mode 1 and mode 2 optical properties are
226 computed every 10 nm from 170 to 320 nm, and for 11 values of $m_i(250 \text{ nm})$

227 ranging from 10^{-4} to 2×10^{-1} .

228 3.4. Fitting strategy

229 3.4.1. Choice of fitted parameters

230 Since SPICAV did not allow for resolving the individual gaseous spectral
231 lines, we are usually able to fit three parameters in our observed spectra in
232 order to account for the three distinctive features in those spectra, namely
233 (a) their spectral average radiance factor; (b) a 215 nm-centered absorption
234 band caused by SO and SO₂; (c) a 280 nm-centered absorption band caused
235 by SO₂ alone. Since we cannot distinguish between SO and SO₂ absorption
236 at SPICAV spectral resolution, we chose the following other three parameters
237 to be fitted: (a) SO₂ abundance at 70 km; (b) cloud top altitude at 250 nm,
238 through the Z_2 control point; and (c) imaginary index of mode 1 particles at
239 250 nm. This choice enables a proper fitting of both absorption bands, since
240 altering Z_2 changes the relative weight of both absorption bands due to the
241 the difference in Rayleigh scattering by CO₂ as well as difference in single
242 scattering albedo of mode 1 particles between 215 and 280 nm.

243 Also, following Frandsen *et al.* (2016), we also considered the possibility
244 of UV contrasts being caused by OSSO, by implementing their analytical
245 cross-section for both cis- and trans-isomers of OSSO, as well as their cal-
246 culated vertical profile. However, we could not obtain satisfactory fits of
247 the observed radiance factors in this way, OSSO absorption having a negli-
248 gible influence over the modeled radiance factor unless unrealistically high
249 abundances (peaking well over 1 ppmv at 62 km) were prescribed, which
250 in this case resulted in the suppression of other spectral features. Follow-
251 ing Krasnopolsky (2018), we therefore claim that the OSSO profile computed

252 by Frandsen *et al.* (2016) cannot account for the UV radiance observed by
253 SPICAV-UV.

254 A fourth parameter, absorption depth near 250 nm caused by ozone, can
255 be measured on a sizable minority of the spectra as extensively discussed in
256 §3.4.2. The analysis of the results obtained for the other fitted quantities
257 will be discussed in another paper.

258 3.4.2. Criterion for O₃ detection

259 The fact that we do have systematic errors that account significantly for
260 our reduced χ^2 values (median value at 28.6 without O₃) prevents us from
261 using a simple difference criterion between χ^2 without considering O₃ and
262 χ'^2 when introducing O₃ as an extra degree of freedom. So we decided to use
263 the more robust *improvement ratio* $r = \chi^2/\chi'^2$ instead.

264 Some observed radiance factors show indeed a distinctive improvement of
265 their reduced χ^2 once O₃ is allowed to vary in the forward model (Fig. 3):
266 for these spectra, it is impossible to reach a satisfactory agreement between
267 observations (high radiance in the 210-230 nm range, concavity near 250 nm)
268 and our forward model without adding O₃ absorption near 250 nm, allowing
269 at the same time for a lower SO₂ and SO absorption. Therefore, in order to
270 distinguish between genuine and spurious detections of O₃, we investigated
271 the improvement ratio for all spectra. The results are shown in Fig. 4. Most
272 spectra actually benefit little from the inclusion of O₃, with a marginal in-
273 crease of r less than 1.5. However, a sizable minority of spectra, especially at
274 latitudes higher than 50°, display r well in excess of 5. In order to avoid false
275 positives (at the expense of discarding some actual detections), we decided
276 to trust our O₃ measurements only if $r > 5.5$, corresponding to a p -value of

277 0.27% (3σ) assuming that the quantity $-2(r - 1)$ (which is reminiscent of
 278 a likelihood ratio test statistics) follows a χ^2 law with one degree of freedom
 279 (corresponding to the additional one parameter, namely O₃ VMR) according
 280 to Wilk’s theorem. Incidentally, a similar value for r was also considered
 281 by Montmessin *et al.* (2011) in their SPICAV-UV occultation detection of
 282 O₃.

283 3.4.3. Probed altitude range

284 Spectroscopic measurements of minor species using backscattered solar
 285 light are sensitive to *column densities* instead of absolute mixing ratios.
 286 Therefore, in order to convert our fitted O₃ mixing ratios into column den-
 287 sities and compare them with values obtained on Earth or Mars (Perrier
 288 *et al.*, 2006), we need to know the penetration depth of backscattered pho-
 289 tons. Monte-Carlo radiative transfer modeling would readily yield such a
 290 quantity, but discrete ordinate radiative transfer solvers (like DISORT) do
 291 not. In order to derive this quantity, we designed the following algorithm:

- 292 1. For a given model atmosphere and wavelength, run our forward model
 293 and store the modeled radiance factor R_0 ;
- 294 2. Replace a given computational layer located at altitude z with an opti-
 295 cally thick and absorbing layer. The resulting radiance factor $R(z)$ will
 296 be $0 < R(z) < R_0$, with $R(z) \rightarrow 0$ as z increases towards the observer,
 297 and $R(z) \rightarrow R_0$ for a deep layer that backscattered photons do not
 298 usually reach;
- 299 3. Locate the altitude z_1 where $R(z_1)/R_0 = 1/2$. This altitude z_1 defines
 300 our effective scattering altitude.

Figure 3: Best fits obtained considering (solid orange) and discarding (solid blue) O_3 . An O_3 -rich observation is shown on upper left panel, marginal O_3 detection in the upper right panel and a non-detection of O_3 on the lower left panel, according to our improvement ratio criterion. Gaseous cross-sections taken into account in our model are shown on the lower right panel.

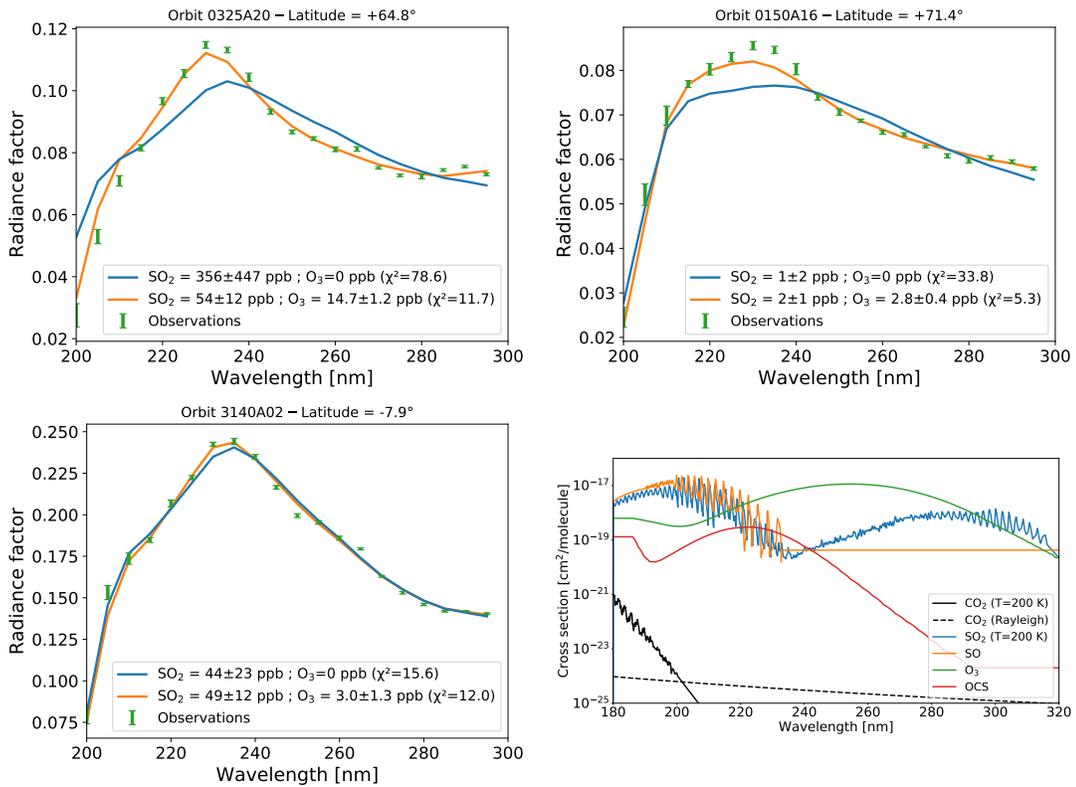
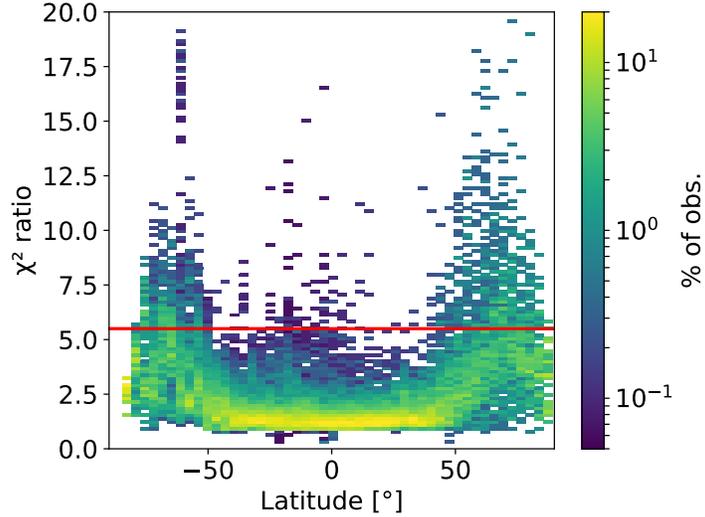
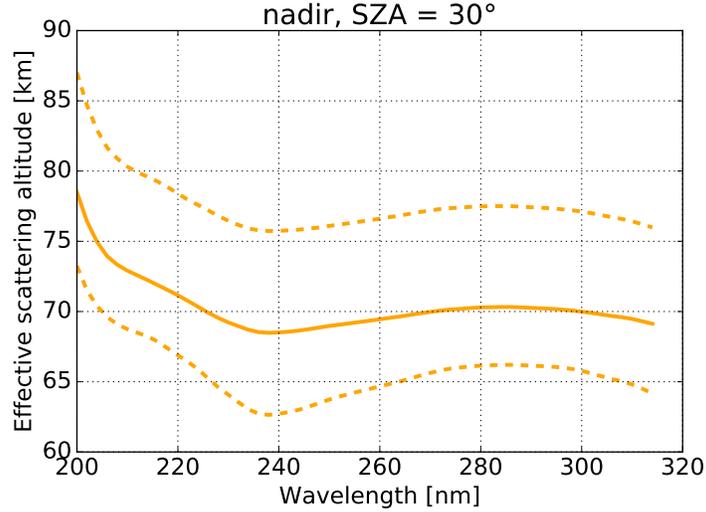


Figure 4: Density plot of χ^2 improvement ratio (without O₃/with O₃) according to latitude. The adopted threshold (5.5) is shown in solid red.



301 This algorithm may even be extended to derive the “optical stiffness” of
 302 the atmosphere: assuming a normal distribution for the backscattering al-
 303 titude, we can compute its 1-standard deviation interval, using respectively
 304 0.5 ± 0.341 as values for $R(z)/R_0$. The resulting effective scattering altitude
 305 distribution is shown in Fig. 5. Shorter wavelengths probe higher in Venus
 306 atmosphere, which is expected considering that they are on the edge of a
 307 strong CO₂ absorption band. For wavelengths longer than 240 nm, the ef-
 308 fective scattering altitude is uniform within ± 2 km, whereas the standard
 309 deviation of scattering altitudes is on the order of ± 5 km, close to the at-
 310 mospheric scale height. We will therefore consider that our model probed
 311 the two scale heights below the cloud top level ($\tau = 1$ at 250 nm is located
 312 at an altitude of 74 km for the computations shown in Fig. 5). Incidentally,

Figure 5: Effective scattering altitude for our typical model atmosphere (solid orange) and $\pm 1\sigma$ deviation (dashed orange).



313 Figure 5 also confirms that the two SO_2 bands centered near 215 and 280 nm
 314 do not probe exactly at the same altitude, with the 215 nm band probing
 315 about 2 km higher on average.

316 4. Results

317 4.1. Observed Ozone distribution

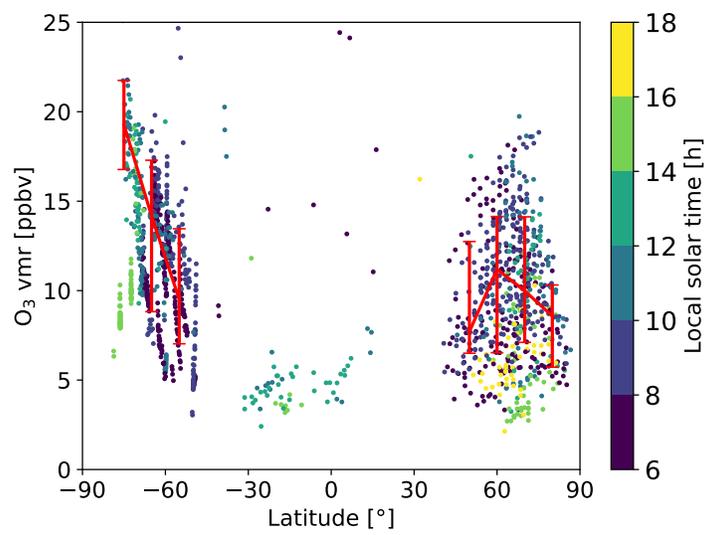
318 First of all, as could already be seen on Fig. 4, Fig. 6 shows that the
 319 overwhelming majority of O_3 detections took place polewards of 50° . The
 320 detection threshold is around 2-3 ppbv in the probed altitude range. The
 321 typical maximal mixing ratio in both hemispheres lies in the 10-20 ppbv range
 322 considering our assumed vertical profile between 55 and 70 km in altitude, the
 323 location of the maximum in the northern polar region being $80^\circ N$, in the cold

324 collar region. Retrievals in the southern hemisphere are less numerous (6.7%
325 of positive detections polewards of 50°S compared with 18.2% of positive
326 detections polewards of 50°N), which is expected since the quasi-polar orbit
327 of *Venus Express* with a pericenter near 78°N made nadir observations of the
328 northern hemisphere easier and more accurate. Keeping this fact in mind,
329 mixing ratios in the southern hemisphere (median and $\pm 1\sigma$ dispersion of
330 $11.4_{-3.3}^{+4.2}$ ppbv) look comparable to those found in the northern hemisphere
331 (median and $\pm 1\sigma$ dispersion of $9.4_{-3.7}^{+4.3}$ ppbv), albeit somewhat higher and
332 without any evidence for a symmetrical peak near 80°S. Detections at lower
333 latitudes are most likely spurious and not significant – about 0.55%, which
334 is close to the expected false positive rate considering our retained 0.27%
335 p -value threshold discussed in §3.4.2. The fact that this cloud top O₃ only
336 exists at high latitudes may explain why it eluded detection until now, since
337 these latitudes are barely observable from Earth due to Venus small axial tilt
338 with respect to the ecliptic.

339 Translated in column densities between 65-70 km (since most backscat-
340 tered photons have not ventured below 65 km, see §3.4.3), these maximal
341 mixing ratios are in the 0.1-0.5 DU range. This is comparable to typical
342 values on Mars out of the dry polar vortices, although one order of mag-
343 nitude less than the maximal values on Mars in the dry polar vortices –
344 typically 4-5 DU according to Perrier *et al.* (2006). It is also three orders of
345 magnitude less than our Earth’s ozone layer – typically 300 DU, which cor-
346 responds to a layer of 3 mm thickness of pure ozone under STP conditions
347 ($1 \text{ DU} \approx 2.69 \cdot 10^{16} \text{ O}_3 \text{ molecules/cm}^2$).

348 Figure 6 may hint at some level of local solar time (LST) variability,

Figure 6: Latitudinal plot of O_3 mixing ratio with respect to latitude. Color codes for local solar time. Solid red lines and error bars stand for running average and statistical dispersions within 5° -wide latitudinal bins.



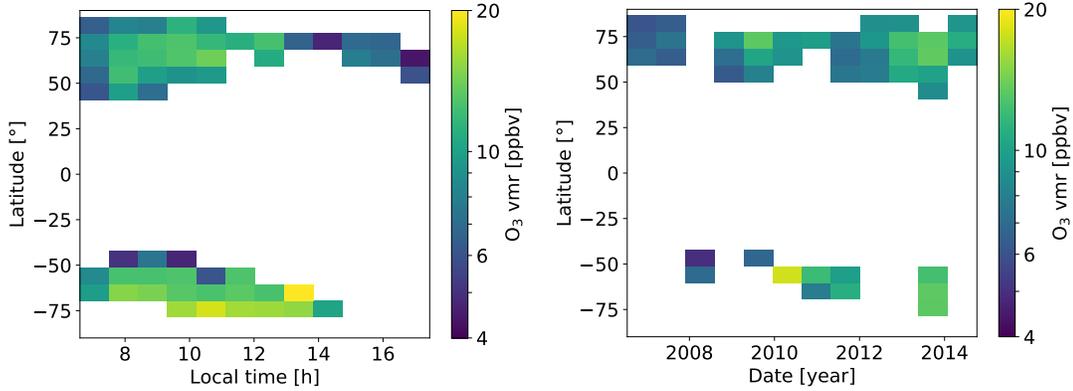
349 at least for higher quality measurements in the northern hemisphere, with
350 more O₃ near the morning terminator than near the evening. However, we
351 must keep in mind that, unlike the daily latitudinal sweeping resulting from
352 the polar orbit, the observed local time only varied slowly, along with the
353 precession of *Venus Express* orbit with respect to sub-spacecraft local solar
354 time. So that it is difficult from our data alone to disentangle local time vari-
355 ability from possible long-term, secular variations. Since no such local time
356 asymmetry is visible for the southern hemisphere measurements in Fig. 6, a
357 weak secular trend is indeed a more likely explanation. Our average maps
358 in Fig. 7 confirm this ambiguity: a morning/evening asymmetry is likely in
359 the northern hemisphere, but alternatively, there could be a slight secular
360 increase of O₃ during the whole *Venus Express* mission. Whether this secu-
361 lar O₃ increase, if genuine, is linked to the known secular variations of cloud
362 top SO₂ (Esposito *et al.*, 1988; Marcq *et al.*, 2013) is a question of interest
363 for future observers and photochemical modelers.

364 4.2. Comparison with general circulation model with photochemistry

365 The existence of a polar ozone layer at the Venus cloud top is theoretically
366 predicted by the LMD IPSL general circulation model (GCM) from Lebon-
367 nois *et al.* (2010). In its version with coupled photochemistry (Stolzenbach
368 *et al.*, 2014), the LMD model shows the formation of a distinct ozone maxi-
369 mum between 55-65 km in both hemispheres poleward of 60° (Fig. 8). Both
370 the altitude and the latitude range of the simulated cloud top ozone lay-
371 ers show a strong similarity with the SPICAV observations, at least from a
372 qualitative point of view.

373 As already diagnosed in the LMD GCM simulations of Lebonnois *et al.*

Figure 7: *Left*: median map of cloud top O₃ with respect to latitude and LST. *Right*: median pseudo-map of cloud top O₃ with respect to latitude and date of observation

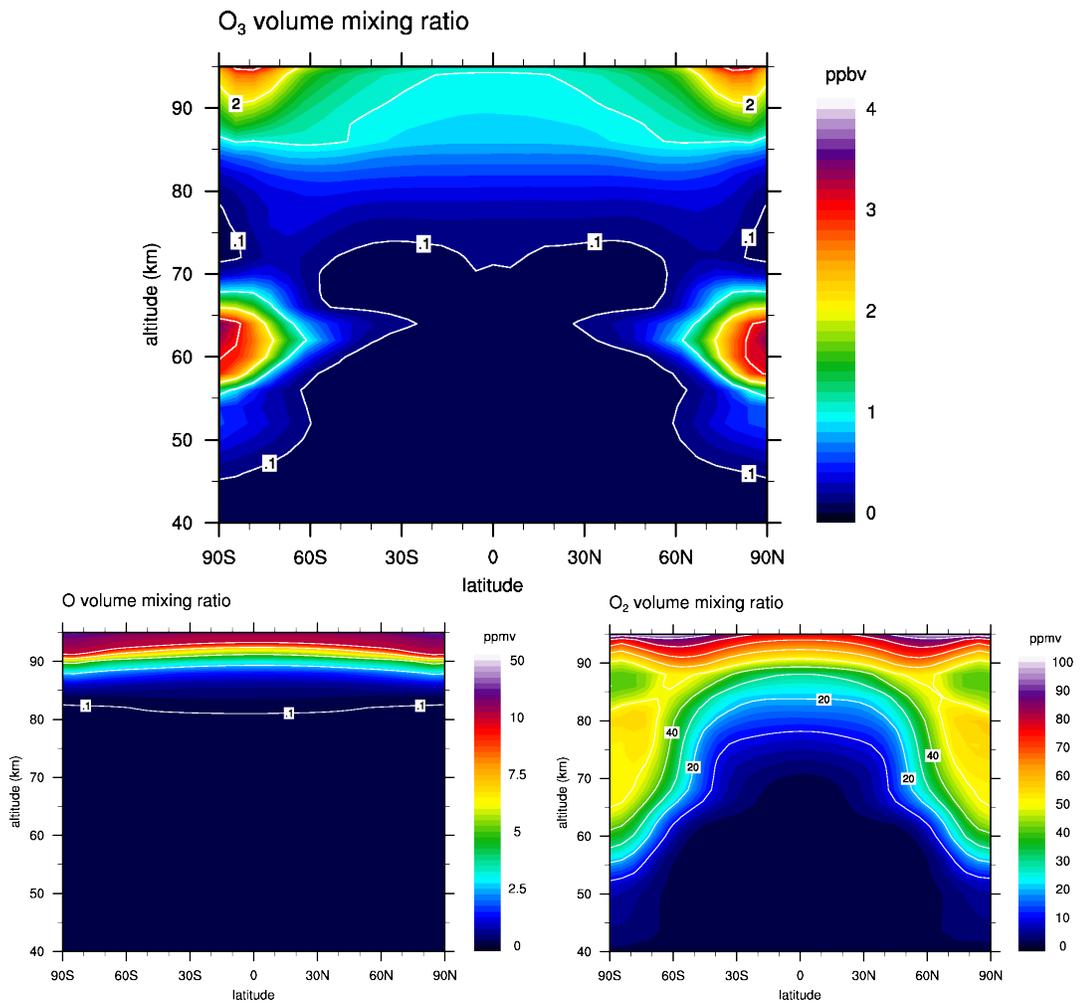


374 (2010), the Venus mean meridional circulation is organized in large-scale
 375 Hadley cells throughout the upper cloud and mesosphere. In this type of
 376 circulation, subsiding motion occurs permanently over both polar regions
 377 and transports chemical species downwards from the upper atmosphere to
 378 lower altitudes. Obviously this process mostly impacts the distribution of
 379 long-lived species, which are little affected by chemical processes and quasi-
 380 conserved during their slow downward transport towards the poles. Figure 8
 381 illustrates the effect of the Hadley circulation on O and O₂. Both species are
 382 essentially produced in the upper atmosphere and are the source species of
 383 ozone through the reaction :



384 Figure 8 shows that the mean meridional circulation has little effect on
 385 the O distribution below 95 km, owing to the short photochemical lifetime

Figure 8: Zonally averaged mixing ratio (ppbv) of O_3 (above), O (lower left) and O_2 (lower right) calculated by the LMD general circulation model.



386 (minutes) of O atoms in this altitude range. In contrast, with a lifetime of
387 several years, O₂ is dramatically impacted by the Hadley circulation. Down-
388 ward transport of upper atmosphere O₂ increases its mixing ratio by one
389 order of magnitude over the polar regions. This ultimately leads to the for-
390 mation of an ozone layer at the cloud top, where the air density becomes
391 sufficiently large to promote the efficiency of the three-body reaction (Eq. 1).

392 Thus, we argue from the LMD GCM simulation that the cloud top ozone
393 detected by SPICAV is a visible signature of the Hadley meridional circu-
394 lation on Venus. This process of ozone formation caused by the deep ver-
395 tical downwelling of oxygen-rich air masses over the pole is similar to that
396 identified on Mars by Montmessin and Lefèvre (2013) using the SPICAM in-
397 strument. Nevertheless, despite a good qualitative agreement, on Venus the
398 mean ozone mixing ratio (about 3 ppbv) calculated by the LMD GCM in the
399 polar layer is smaller by a factor of five than the ozone retrieved from SPI-
400 CAV observations. This suggests that the GCM underestimates the amount
401 of O₂ mixing ratios that are present near the poles at the cloud top. Al-
402 ternatively, the ozone loss mechanisms by sulfur and chlorine species might
403 be overestimated in the model. We should however note that our retrieved
404 O₃ mixing ratio is very dependent on the assumed vertical profile. In any
405 case, the reasons for this quantitative discrepancy will be investigated in a
406 forthcoming study.

407 *4.3. Comparison with previous O₂ measurements*

408 The observed existence of cloud top O₃ implies that its precursor species
409 O₂ is also present, as can be seen in Fig. 8 above, with a typical high latitude
410 mixing ratio of 50 ppmv near cloud top. These values are well in excess of the

411 previously known O₂ upper limits (Marcq *et al.*, 2018) of about 2 ppmv above
412 300 mbar, which are based on near infrared high-resolution spectroscopic
413 observations of Venus day side by Mills (1999) using UHRF/AAT.

414 We therefore investigated those O₂ upper limit measurements and we
415 found that all of their observations were restricted to latitudes lower than 50°
416 – slit offset of 0.5 to 0.7 Venus radii from the observed disk center according
417 to Mills (1998). At these relatively lower latitudes, the LMD-GCM does
418 not predict any significant O₂ in the 50-70 km altitude range (Fig. 8), nor
419 do we observe any O₃ (Fig. 6). Therefore, we claim that our O₃ discovery
420 remains consistent with known observational limits on its source species O₂.
421 Furthermore, if O₃ – and therefore O₂ – abundances are subject to secular
422 variations, as suggested in Fig. 7 (right), it is also possible that Mills (1999)
423 measurements were performed at a time of relative O₂ scarcity.

424 5. Conclusion

425 We have collected robust observational evidence for a newly discovered
426 ozone layer in the upper clouds of Venus, restricted to latitudes higher than
427 50° in both hemispheres. These findings do not contradict previous obser-
428 vational constraints (restricted to lower latitudes). Due to its dynamical
429 formation mechanism, this ozone layer was not predicted by 1D photochem-
430 ical models. On the other hand, such a high-latitude ozone layer is predicted
431 by our 3D photochemical model (Stolzenbach *et al.*, 2014), which indicates
432 that this O₃ layer is formed through a mechanism similar to that found in
433 the Martian upper atmosphere (Montmessin and Lefèvre, 2013). The Venus
434 polar ozone layer is however about 10 times thinner than on Mars in terms of

435 observable column densities (0.1 to 0.5 DU), with no obvious seasonal effect
436 and/or temporal trend in this case.

437 This discovery also strengthens the argument against using the sole O₃
438 detection as a proxy for planetary habitability, since even in our own solar
439 system, O₃ is found in the 1 to 10 mbar pressure range in all three telluric
440 atmospheres, although two out of three (Venus and Mars) do not meet the
441 usual criteria for planetary habitability. Actually, in order to protect surface
442 life from harmful stellar UV radiation, one has to find at least ~ 100 DU of
443 ozone in the atmosphere of a planet or exoplanet. In the solar system, only
444 Earth exceeds this value.

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448 Science Archives (PSA) both the day side nadir UV albedo spectra and the
449 columns of SO₂ and ozone derived from SPICAV/Venus Express mission.
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