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# First detection of O<sub>2</sub> 1.27 $\mu$ m nightglow emission at Mars with OMEGA/MEX and comparison with general circulation model predictions

J. L. Bertaux,<sup>1</sup> B. Gondet,<sup>2</sup> F. Lefèvre,<sup>3</sup> J. P. Bibring,<sup>2</sup> and F. Montmessin<sup>1</sup>

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[1] We report the first detection in the atmosphere of Mars of the nightside O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ) emission at 1.27  $\mu$ m from limb observations of the OMEGA imaging spectrometer on board Mars Express (MEX). The emission, detected in three cases out of 40 observations, is due to recombination in a downwelling air parcel of O atoms produced by photodissociation of CO<sub>2</sub> on the dayside in the upper atmosphere ( $O + O + M \rightarrow O_2^* + M$ ), and not from ozone UV photodissociation, as is often seen on the dayside. Observed vertical profiles and total retrieved vertical intensities are compared with models. When detected, the emission is 10 times larger than previous predictions, at  $\sim 240$  kR. This can be explained in the frame of a general circulation model (GCM) of Mars. As predicted by the GCM, all positive observations were obtained at high latitudes, during the winter night. The model is validated, which simulates the large Hadley cell characterizing the meridional circulation, ascending from the summer pole and descending to the winter pole. This new emission is tracing uniquely a downward advection transport mechanism, and therefore its detailed study will provide important constraints on the overall aeronomy and dynamics of Mars. The impact on long-term stability of methane is examined. It is found that recycling through the mesosphere will not decrease significantly the overall lifetime of CH<sub>4</sub> ( $\sim 300$  years), because the descent of air is confined to high latitudes and winter seasons. These observations are demonstrating a new diagnosis of the aeronomy and atmospheric dynamics of Mars.

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## 1. Introduction

[2] Natural atmospheric light emissions are revealing physical and chemical processes that govern the aeronomy of a planetary atmosphere, and therefore their observations are excellent candidates to be compared to models, for a better understanding of its complex machinery and long-term stability. In the upper atmospheres of both Venus and Mars, CO<sub>2</sub> and N<sub>2</sub> molecules are photodissociated with a production of O and N atoms in the thermosphere ( $z > 80$ – $90$  km) on the dayside. The thermospheric circulation of Venus is characterized by a strong flow from the sub solar point to the anti solar point; in the descending air parcel on the nightside, atoms of O and N are recombining,

and produce both ultraviolet NO emission nightglow (Feldman *et al.* [1979] with Pioneer Venus and Gérard *et al.* [2008] with Venus Express) and near infrared O<sub>2</sub> at 1.27  $\mu$ m (discovered from ground based observations by Connes *et al.* [1979] and excellently mapped from Venus Express [Drossart *et al.*, 2007; Gérard *et al.*, 2009b]). While the NO emission was already detected in the atmosphere of Mars by SPICAM on Mars Express [Bertaux *et al.*, 2005] the O<sub>2</sub> nighttime emission had not been reported up to recently at Mars [Gondet *et al.*, 2010], from observations of OMEGA also on board Mars Express.

[3] The recombination of O atoms requires a third body (mainly CO<sub>2</sub> on Mars and Venus) and produces excited molecular oxygen O<sub>2</sub><sup>\*</sup>:



Reaction (1) produces O<sub>2</sub><sup>\*</sup> in seven different electronic states leading to a series of complex energy transfer processes by emission of radiation or by quenching (for an excellent review, see Krasnopolsky [2011]). Quantitative assessments of these transitions between the excited states of O<sub>2</sub><sup>\*</sup> have been made by Crisp *et al.* [1996] and Krasnopolsky [2011], who have estimated the net effective yield of the O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ )

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**Table 1.** OMEGA Observations Conditions<sup>a</sup>

Orbit	Date	L <sub>s</sub>	Latitude	Longitude	Local Time	Solar Zenith Angle	Time Since Sunset	Peak Altitude (km)	Peak Intensity (MR)
1084	22 Nov 2004	118°	76.5°S	13.5°E	16:10	107°	155 sols <sup>b</sup>	42	12
1619	21 Apr 2005	197°	70°N	164°E	21:50	115°	4 h, 30 min	43.5	9.3
2623	27 Jan 2006	2.8°	85°S	120°E	03:40	95°	0	49	17

<sup>a</sup>Parameters describing the three OMEGA observations of the nighttime O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission are the Mars Express orbit number; date; latitude and longitude of the observation; local time; solar zenith angle; time since sunset (defined as sza = 95°); and altitude and intensity of the observed peak of emission.

<sup>b</sup>One sol is one Martian solar day (24.6 h).

state in reaction (1) to be 0.7–0.75 on Mars and Venus. The O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) then de-excites spontaneously with a time constant of about 1.2 h and the emission of one 1.27  $\mu$ m photon: O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub> → X<sup>3</sup>Σ<sub>g</sub>), or may be quenched by collisions.

[4] Let us consider an air parcel that has been exposed to daylight and photodissociation by solar UV ( $z > 90$  km). For a given mixing ratio  $\mu = [\text{O}]/[\text{CO}_2]$ , the reaction rate of recombination (1) (per cm<sup>3</sup> s) is proportional to  $[\text{O}][\text{O}][\text{CO}_2] = \mu^2 [\text{CO}_2]^3$ , containing the third power of CO<sub>2</sub> density. At high altitude, [CO<sub>2</sub>] is small and the motion of an air parcel is done with  $\mu$  approximately constant. While an air parcel is descending through advection, [CO<sub>2</sub>] increases and O atoms are recombining more and more, until exhaustion of O atoms.

[5] There is another mechanism which produces the same 1.27  $\mu$ m emission: photo-dissociation of ozone by solar UV on the dayside, which was first detected on Mars from ground based observations [Noxon *et al.*, 1976], and monitored from orbiters like Mars Express as a useful mean to quantify ozone [Fedorova *et al.*, 2006; Zasova *et al.*, 2006] or from ground based telescopes by Krasnopolsky [2003]. In his study of this 1.27  $\mu$ m ozone dayglow emission from the Infrared Telescope Facility at Mauna Kea, Krasnopolsky [2003] detected some emission in the small night crescent as seen from Earth, but concluded that it was either some optical contamination from the dayside within the telescope point spread function, or a remnant of the ozone-induced emission lasting some time after crossing the evening terminator. We argue in the following that the observations of OMEGA with a positive detection of the night O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission, performed in the winter polar night, are not due to ozone photo-dissociation or its remnant but to oxygen recombination, yielding its first non-ambiguous detection.

## 2. Observations With OMEGA

[6] OMEGA is a VIS/NIR hyperspectral imager operating on board of the ESA/Mars Express mission [Bibring *et al.*, 2004]. The instrument is made of two co-aligned channels: a pushbroom “VIS” channel acquires up to 128 spectra (from 0.35 to 1  $\mu$ m) simultaneously on a CCD matrix; a NIR channel (1 to 5.1  $\mu$ m) operates in whiskbroom mode (scanning mirror across track), with two linear InSb detectors (128 pixels each), and 14 nm spectral sampling in the range 1 to 2.5  $\mu$ m. Nadir and limb pointing can be implemented. OMEGA identifies and maps both surface (minerals, ices, frosts) and atmospheric (gas, aerosols, clouds) species, with in particular CO<sub>2</sub>, CO, H<sub>2</sub>O and O<sub>3</sub> gaseous detections. The 1.2 mrad IFOV corresponds to a footprint from 0.3 to 4 km (depending on S/C altitude or distance to the limb.) Up to

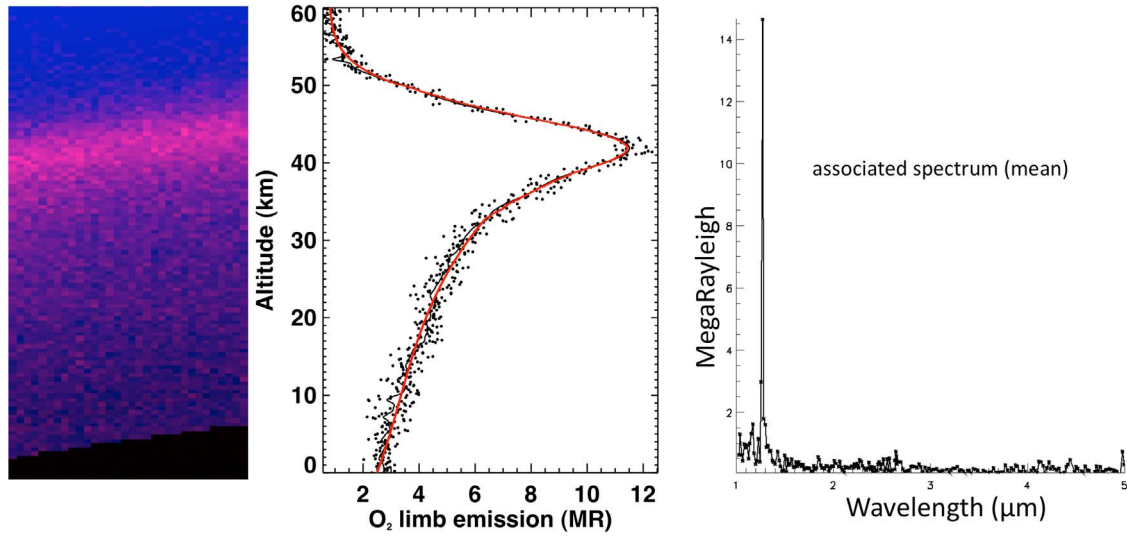
2010, OMEGA has observed the atmosphere 40 times above the limb at night. In three cases out of 40, an intense emission at 1.27  $\mu$ m was detected. Table 1 summarizes the parameters of the three cases with a positive detection. We discuss each of them separately, since they differ in some respects.

### 2.1. Observation at Orbit 1084

[7] Figure 1 illustrates the observation obtained at orbit 1084. When the spatial scan is averaged in altitude, a vertical profile of the emission displays a peak emission of 12 megarayleigh (MR) at an altitude above the areoid (a reference equipotential surface) of 42 km. The spectrum (Figure 1, right) shows the conspicuous O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) line at 1.27  $\mu$ m while the rest of the spectrum remains devoid of any detectable emission. At the latitude (76.5° S) and season (L<sub>s</sub> = 118°) of this observation, the observed air parcel is never illuminated over a diurnal cycle, and therefore, the emission cannot be a remnant of the ozone photo-dissociation process.

[8] For comparison to our observations, the LMD general circulation model (GCM) with coupled chemistry [Lefèvre *et al.*, 2004] was run with the implementation of the calculation of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission over a full Martian year. The emissivity (in photons/cm<sup>3</sup> s or kR/km) was integrated vertically, zonally averaged, and plotted as a function of season and latitude in Figure 2 in units of MR (10<sup>12</sup> photons/cm<sup>2</sup> s). The emission triggered by reaction (1) is present only at high latitudes, is absent during summer, and not perfectly symmetrical between North and South. Pink stars represent the three places and times where OMEGA detected the emission. They are located in the regions/seasons where emission should occur according to the GCM, while locations with no measurable emission are represented by white stars and are indeed located in areas where no emission is predicted. It can be remarked that, according to the model, the emission is present over an extended period of the Martian year, being absent only during summer. At both equinoxes, the model predict some emission in the two polar regions simultaneously, and indeed one of the observation (at orbit 2623) was obtained at L<sub>s</sub> = 3°, during northern spring equinox. The model shows a larger intensity (stronger vertical descent) on both poles at the equinox L<sub>s</sub> = 180° than at L<sub>s</sub> = 0°.

[9] The vertical profile of the intensity measured at the limb (Figure 1) was inverted to retrieve the vertical distribution of the local emissivity (in kR/km), for comparison with the model prediction (Figure 3). Both data and model indicate that the emission is constrained to a finite layer above 40 km, which can be explained qualitatively by the fate of a downwelling air parcel containing O atoms: at high altitude, the CO<sub>2</sub> concentration is too small to get a

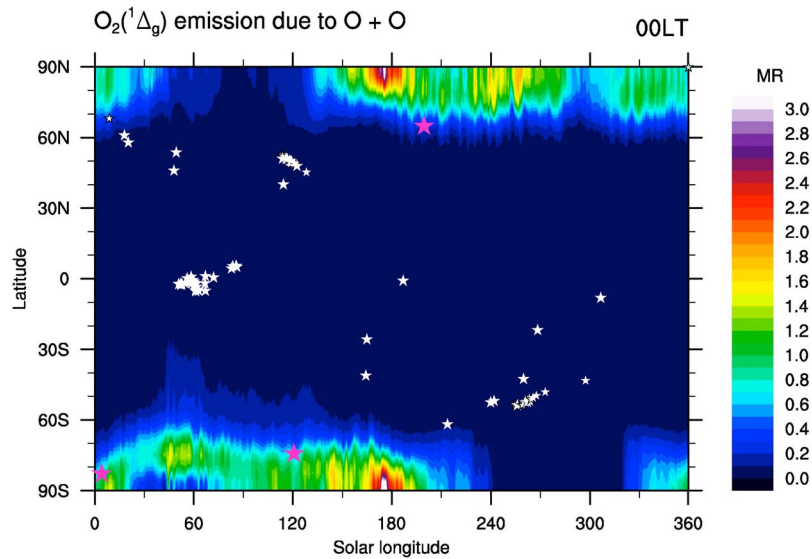


**Figure 1.** (left) A 2.2° wide swath of the observed limb at night by OMEGA, with emission coded in pink. (middle) Vertical distribution of the intensity observed, in MR (integration over azimuth). The red line is a smoothed version of the distribution. (right) Integrated observed spectrum, showing emission only at 1.27  $\mu$ m.

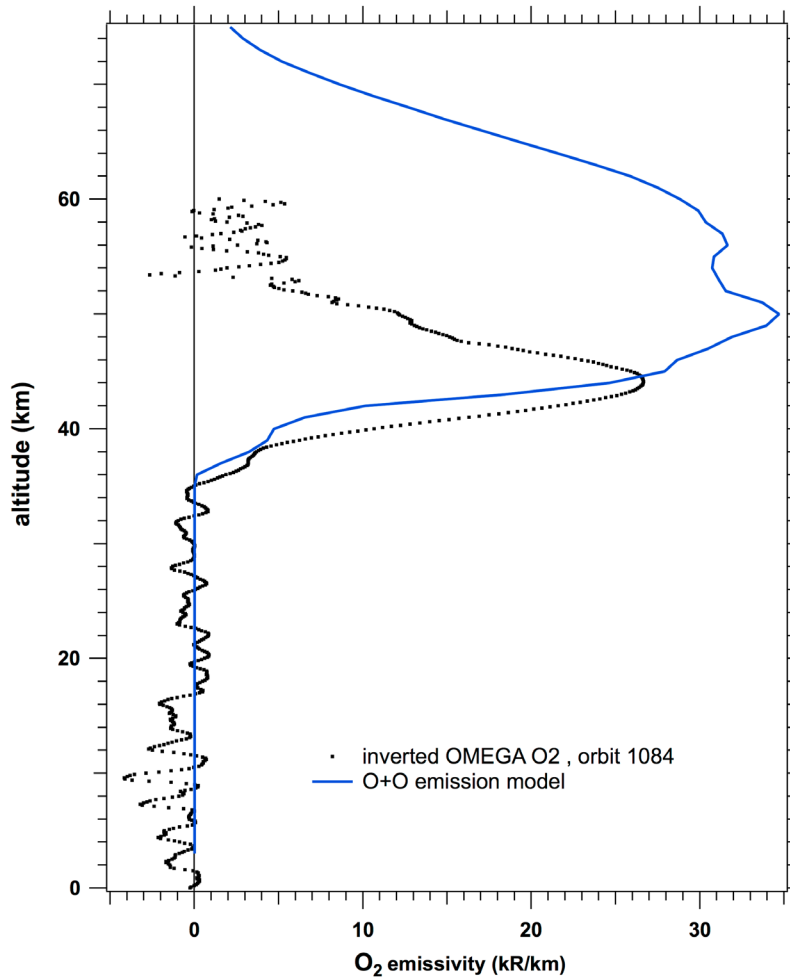
significant reaction rate for reaction (1). Then, [CO<sub>2</sub>] is increasing by compression and the recombination of O atoms takes place with a corresponding emission. Further down, there are no more O atoms to fuel reaction (1).

[10] Though the two profiles (data and model) have a comparable morphology, they differ significantly in several aspects. The observed peak emissivity is slightly weaker than predicted by the model (26 instead of 34 kR/km). The vertical emission intensities (obtained from vertical integration of profiles of Figure 3) are respectively 0.24 and 0.78

MR for the data and the model. The observed layer thickness of the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission is 8.3 km (at half-maximum value) instead of 23 km in the model (which explains the lower observed vertical emission); it extends from 40.5 km to 49 km (at half-peak), while the model layer extends from 43 to 66 km. Therefore, the mid altitude of the layer is lower in the observation than in the model (42 km versus 54 km), and there is a lack of measured emissivity above ~52 km, where the model predicts still a substantial emission. The observed peak altitude of 42 km is much lower than the NO



**Figure 2.** Zonally averaged O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) vertical emission produced by the O + O recombination (MR), as calculated by the LMD general circulation model. Locations where OMEGA detected an emission (three pink stars) are in the regions where the model predicts a substantial intensity, while observations without detection (white stars) are outside these regions. The emission is predicted only at latitudes higher than 60°, over a rather extended season centered on peak winter, and absent during peak summer. At both equinoxes, the model predicts simultaneous emission in both polar regions.



**Figure 3.** Comparison of OMEGA O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) local emissivity at 1.27  $\mu$ m (in kR/km) at orbit 1084 with the LMD GCM prediction for  $L_s = 120^\circ$ , latitude =  $76.5^\circ$ S. For this particular condition of observation, the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission at 1.27  $\mu$ m calculated by the model is entirely due to the O + O reaction (the contribution of the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission triggered by O<sub>3</sub> photodissociation, not shown, is equal to zero).

peak emission [Cox *et al.*, 2008, 2010] at  $\sim 70$  km, a feature similar to the situation on Venus, where in average the peak emissions are found at 97 and 113 km respectively for O<sub>2</sub> and NO [Gérard *et al.*, 2009a]. It is important to note that for this particular condition of observation, the model shows that no emission at 1.27  $\mu$ m is expected from a night remnant of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) produced by O<sub>3</sub> photodissociation (not shown here).

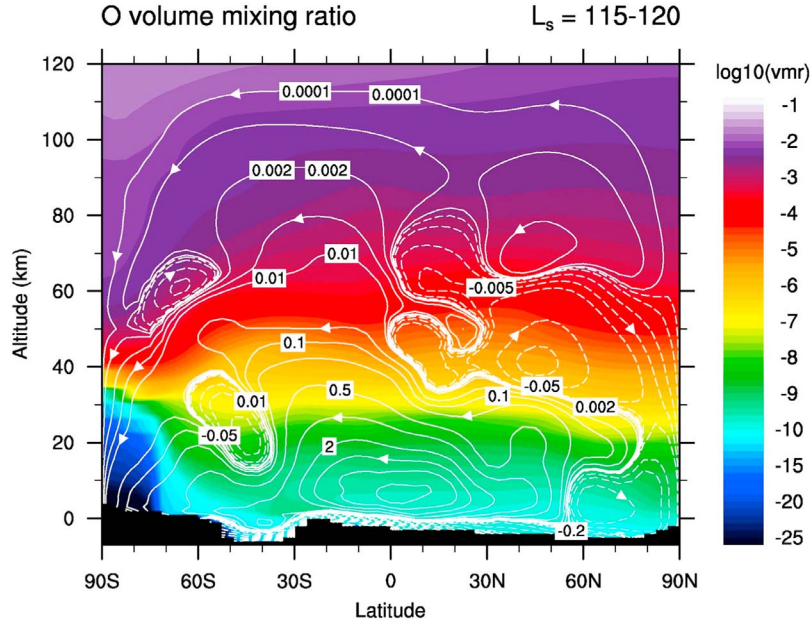
[11] In Figure 4 is represented the model zonally averaged distribution of O atoms relevant to the season  $L_s = 115\text{--}120^\circ$ . Superimposed are the isolines of the mass stream function, describing the atmospheric general circulation in latitude-altitude. Atomic oxygen is produced above 80 km and is transported downward in the descending branch of the Hadley cell above the south pole, where recombination of O atoms occurs. The strong deficit of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission observed by OMEGA relative to the model above 52 km is possibly indicative of a slab of air of different origin than predicted by the GCM, perhaps coming from a lower altitude poorer in O, as suggested by the meridian field of the distribution of O atoms of Figure 4.

## 2.2. Observation at Orbit 1619

[12] Conditions of observations for the detection at orbit 1619 are indicated in Table 1. Figure 5 displays the 1.27  $\mu$ m signal observed by OMEGA at orbit 1619 at the limb, and the result of the vertical inversion (emissivity, or local emission in kR/km), assuming that the emission vertical profile is spherically symmetric. It displays two peaks of emission. The main peak of the emission is at 43 km with 8 MR, and the main peak of the emissivity is at 45 km. The vertically integrated emissivity gives a vertical emission rate of 0.15 MR. The observation was taken at  $L_s = 197^\circ$ , latitude  $70^\circ$ N and  $164^\circ$ E, local time = 21:50 (Table 1).

[13] The secondary peak around 25 km of projected altitude is most likely an artifact of the vertical inversion. Remember that the altitude at the limb is the projected altitude of the emitting object in the plane of the limb, and is only an apparent altitude (Figure 6). The true altitude is always equal or larger than the apparent altitude. We believe that the emission of the lower peak takes place at the same altitude as the main peak, but is in the foreground (or background, after the limb). At this place, the emission must





**Figure 4.** Zonally averaged distribution of the atomic oxygen volume mixing ratio calculated by the LMD general circulation model at  $L_s = 115\text{--}120^\circ$ . Superimposed are the isolines of the mass stream function ( $10^9 \text{ kg s}^{-1}$ ), describing the atmospheric general circulation. Around solstices, a large Hadley cell brings air ascending from summer pole (here, North) to the opposite winter pole, where it descends, producing the O<sub>2</sub> nightglow through recombination of O atoms.

be brighter than at the limb, but looks fainter because of the shorter slant path through the emitting layer, as sketched in Figure 6.

[14] We have performed the following exercise. We kept only the part above 40 km in the emissivity vertical profile obtained in Figure 5 (right), and computed what would be the observed emission at the limb if the layer were spherically symmetric. The result is plotted as a red solid curve in Figure 7 (left), while the ratio of actually observed/recomputed is plotted in Figure 7 (right). It is seen that there is a deficiency of emission between 10 and 18 km, and 28–40 km apparent altitude. This deficiency indicates that the layer cannot be horizontally homogeneous. There is also a pronounced excess at 18–28 km apparent altitude.

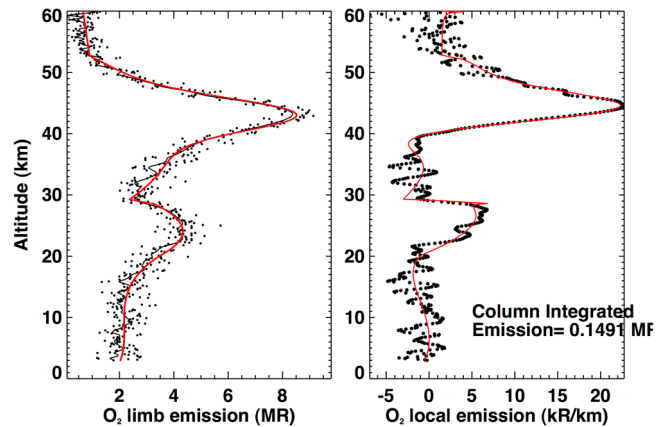
[15] It is possible to retrieve some information on the horizontal variation of the layer's brightness. Assuming that the vertical profile *shape* is constant, but its emissivity modulated by a factor varying horizontally, we can retrieve this factor (taken as the vertically integrated emission), displayed in Figure 8. Of course, we cannot distinguish what is background (after the limb) and foreground (before the limb). At this season, the polar dust layer top is quite low in altitude, and the atmosphere is probably transparent down to 10–15 km. At any rate, it shows that there must be a reinforcement of the emissivity at 300–400 km from the limb, with a typical size of  $\sim 100$  km. It shows that the typical scale of horizontal inhomogeneities of the O<sub>2</sub> layer emission is of the order of 100–300 km.

### 2.3. Observation at Orbit 2623

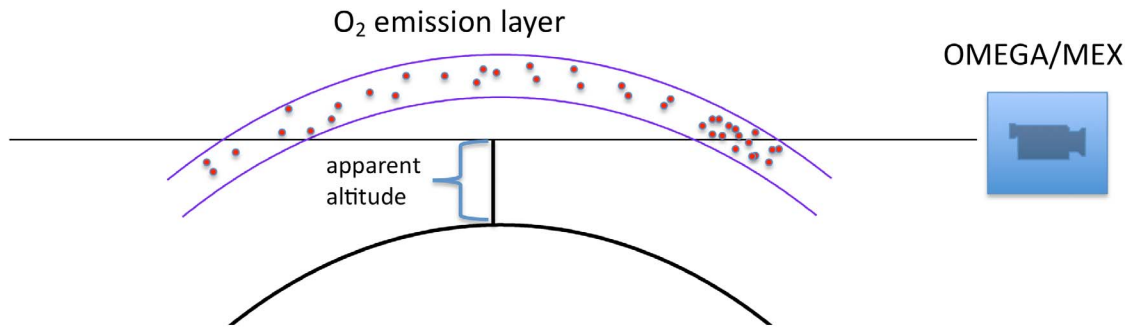
[16] The O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ) nightglow observation of orbit 2623 took place near Northern Spring equinox (Table 1), at high southern latitude (85 S) and 03:40 Local Time. Figure 9

displays the vertical distribution of the O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ) emission and the OMEGA spectra taken at 48 and 23 km. The lower part of the profile shows, in addition to the O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ) emission, a continuum of solar light scattered by aerosols, with also a substantial emission at 1.27  $\mu$ m, on top of the continuum.

[17] Figure 10 shows the OMEGA observation and the GCM prediction for the two processes producing O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ), that is the O recombination (reaction (1)) and the



**Figure 5.** (left) Vertical distribution of the 1.27  $\mu$ m signal observed by OMEGA at orbit 1619 at the limb (all data points, and two versions of smoothing in black and red lines). (right) Result of the vertical inversion (emissivity, or local emission in kR/km), assuming that the emission vertical profile is spherically symmetric (horizontally homogeneous).



**Figure 6.** Schematic of a nonspherically symmetric O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission layer. Red dots represent the emitting O<sub>2</sub> molecules. An excess of emission is schematized in the foreground along the line of sight. The actual altitude of this excess is always larger than the projected (apparent) altitude at the limb. The integrated emission at the point of excess may be fainter than the peak corresponding to the layer, because of shorter slant path through the layer.

photodissociation of ozone. The model peak altitude is slightly above the data peak altitude (4–5 km). The peak intensity is also higher in the model ( $\sim$  factor 2). The model shows that the highest peak corresponds mostly to the recombination of O atoms, while the emission below 36 km is essentially due to the photodissociation of ozone. There, the model shape is different from the observation, which may be due to some horizontal inhomogeneities in the ozone field.

[18] However, it is interesting to see that the model predicts a small secondary layer of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission due to O<sub>3</sub> photodissociation at 50–60 km of altitude. What is the source of this secondary layer? One may speculate that O atoms, when descending in the polar night, also recombine with O<sub>2</sub> molecules (either from background, or freshly formed O<sub>2</sub> molecules) to produce ozone. Indeed, it was recently realized that there is a detached layer of ozone at 40–60 km detected at night in polar regions by UV/stellar occultations from SPICAM/Mars Express [Montmessin *et al.*, 2011a]. These authors argue that this ozone layer is formed through transport of O atoms from the summer pole to the winter pole, exactly as the formation of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) molecules, therefore having a dynamical origin rather than a photochemical source. It is also with the same process that ozone was discovered recently in the atmosphere of Venus [Montmessin *et al.*, 2011b] with SPICAV on Venus Express.

[19] Therefore, once there is O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) formation and 1.27  $\mu$ m emission through air descent, there is also formation of ozone. Even if the descent takes place on the nightside, if this parcel of air is near the terminator (as it may occur near equinoxes), it may be sun-lighted, and the ozone photodissociation will also produce the 1.27  $\mu$ m emission.

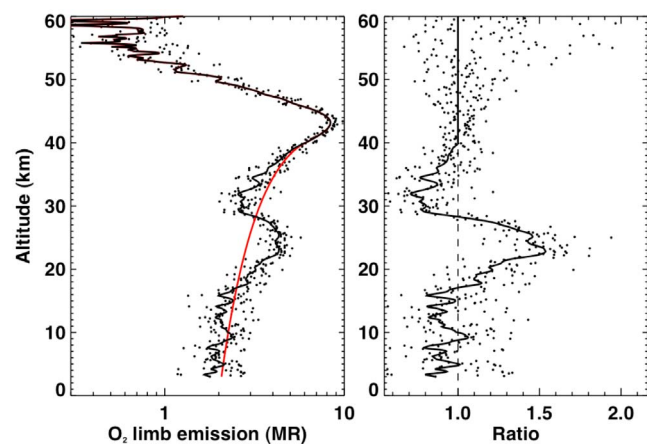
### 3. Discussion

#### 3.1. Comparison Data/Model

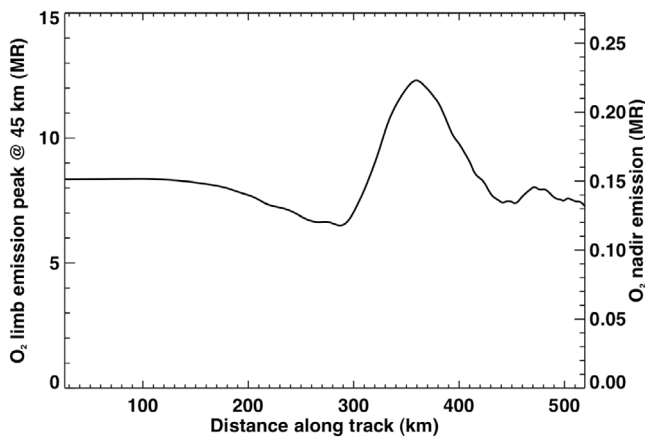
[20] When comparing our data to the present GCM model and previous theoretical predictions, one has to keep in mind that the sensitivity limit of OMEGA is about 1.2 MR looking horizontally, corresponding to a vertical emission of 25 kR. Garcia Muñoz *et al.* [2005] estimated this nighttime emission at 25 kR with a model calculation, 1D and time dependent, latitude 20° with a peak altitude of 62 km. All the

OMEGA observations with non-detection are compatible with this low latitude prediction. Only in the case of high latitude observations, OMEGA sees a much stronger signal, with a lower peak altitude at 42 km. A similar type of 1D model [Krasnopolsky, 2006, 2011] predicts a vertical emission of 13 kR, also fully compatible with the cases of non-detection by OMEGA. In fact, it seems that only general circulation models, which allow a more realistic description of the mean meridional circulation, are able to capture the cases of large nighttime emission, when and where thermospheric air is descending in altitude above the poles.

[21] Comparison of observations with the present GCM shows great similarities in season/latitude dependence, overall validating the model but there are also some significant differences: the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) nightglow measured by OMEGA has a smaller intensity than calculated by the model, and there is no emission detected above 50 km. Accordingly, the observed peak altitude is lower than in the



**Figure 7.** (left) Vertical profile of the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission observed at orbit 1619 in log scale. The red curve is what would be observed at the limb if the layer were spherically symmetric, with an emissivity vertical profile obtained by inversion of the emission observed above the apparent altitude of 40 km. (right) Ratio of observed to a spherically symmetric model (red curve).



**Figure 8.** Reconstructed horizontal variation of the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) nadir emission (scale at right) as a function of distance to the limb, implied by the secondary peak in the vertical profile of the emission at orbit 1619. The scale at left indicates what the corresponding peak emission would be if observed at the limb, proportional to the nadir emission.

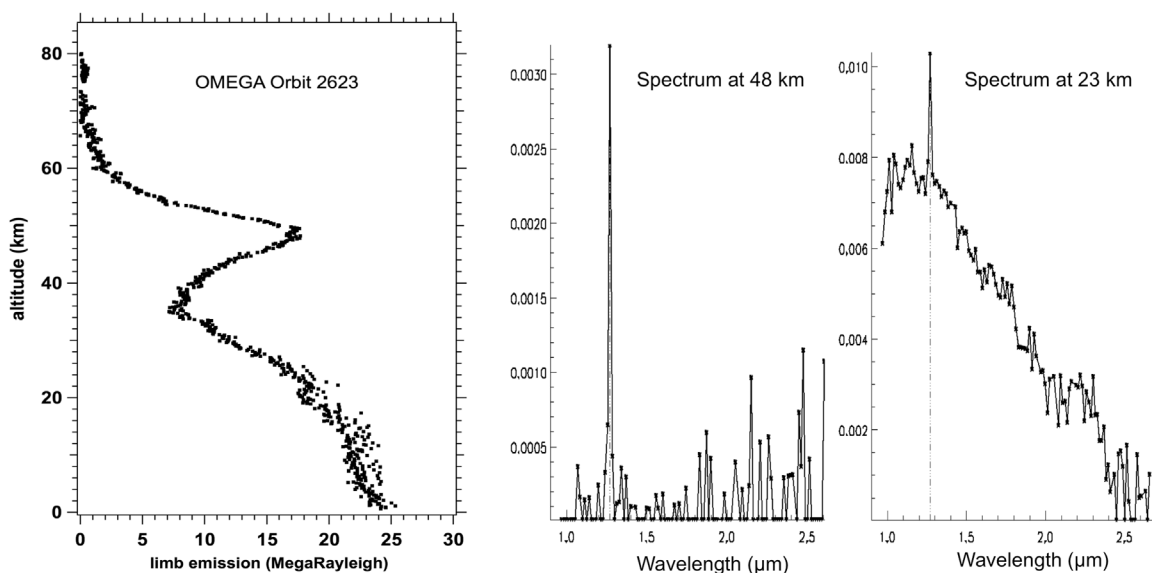
model, by  $\sim 6$  km for orbit 1084 (46 versus 52 km), and  $\sim 5$  km (48 versus 53 km) for orbit 2623. For orbit 1619, there are some horizontal inhomogeneities that precludes a direct comparison. The intensity discrepancies may be due to day-to-day meteorological variability of the upper atmosphere of Mars, or to the rate of reaction (1) adopted in the model, which is still uncertain at the low temperatures (140–170 K) typical of the Martian polar night. Here the GCM employs for reaction (1) the exponential law given by Roble [1995], which is constrained by the laboratory measurements of Campbell and Gray [1973] at 298 K and 196 K. The rate was then multiplied by 2.5 to account for the higher efficiency of CO<sub>2</sub> as a third body [Nair et al., 1994].

[22] In any case, the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) nightglow at 1.27  $\mu$ m is tracing the descent of air originating in the altitude region of CO<sub>2</sub> photo-dissociation (say,  $>80$ –90 km). Therefore, Figure 2 maps the air descent latitude/season pattern of mesospheric/thermospheric origin. It is worth noting that the model predicts that at equinoxes ( $L_s = 0$  and  $180^\circ$ ), there is some emission in both polar areas, indicating that the meridional circulation is divided into two Hadley cells, with descending branches at both poles. Indeed, OMEGA observations at orbits 2623 ( $L_s = 3^\circ$ ) and 1619 ( $L_s = 197^\circ$ ) are confirming this prediction.

### 3.2. The Case of CH<sub>4</sub> Actual Lifetime

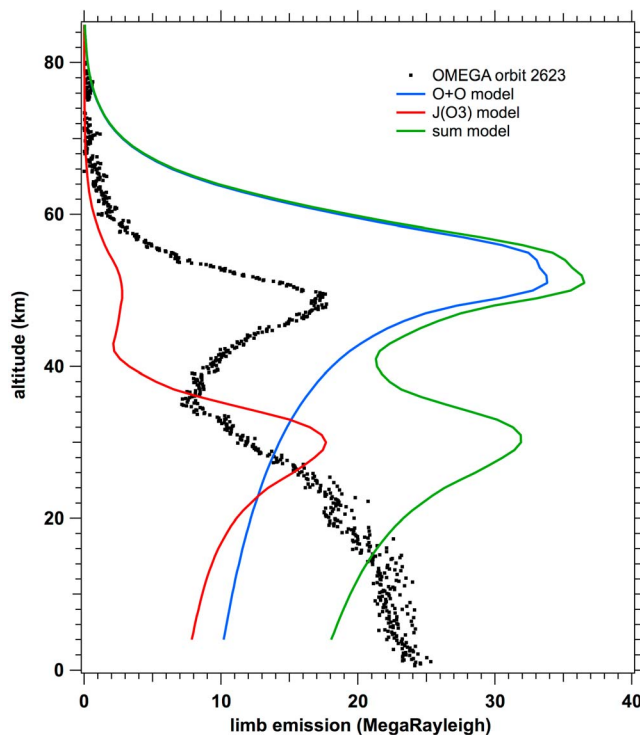
[23] The recent detections of methane [Formisano et al., 2004; Mumma et al., 2009] on Mars have posed a number of issues, in particular the incompatibility between the theoretical chemical lifetime (300 years) and the observation of temporally and spatially sharp changes of the molecule [Lefèvre and Forget, 2009]. We wondered if the observation of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission, linked to a downward flow of air, could give some indication of the time required to recycle the whole atmosphere above  $\sim 70$  km of latitude, where molecules are no longer protected from UV radiation by CO<sub>2</sub>. In particular, the actual lifetime of a given molecule may differ from the one calculated at ground level, according to the rate of recycling of the whole atmosphere through the mesosphere/thermosphere, where it is exposed to the full UV solar radiation. For example, methane (the lifetime of which is  $\sim 300$  years at low altitude) is photodissociated by solar UV radiation in the same spectral region ( $\lambda < 150$  nm) as CO<sub>2</sub> which acts as a shield in the lower atmosphere. At high altitudes above 70 km, the screening effect of CO<sub>2</sub> is much weaker and the methane lifetime is correspondingly shorter (one week).

[24] The present GCM that we use for comparison with the observations simulates the transport of atmospheric constituents by pure advection, with no eddy diffusion. A



**Figure 9.** (left) Vertical distribution of the 1.27  $\mu$ m signal observed by OMEGA at orbit 2623 above the continuum. (middle and right) Spectra obtained at 48 and 23 km of apparent altitude. There is a continuum of solar light scattered by aerosols in the lower part of the observation.





**Figure 10.** Comparison of OMEGA O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission at 1.27  $\mu$ m recorded at orbit 2623, near spring equinox and latitude 85°S, with the LMD GCM prediction for such place and date. In blue is the contribution of the O + O recombination process; in red is that of the photodissociation of ozone. The green curve is the sum of both contributions. In the model the O + O recombination dominates at high altitudes, while the ozone photodissociation is equal to the recombination below 33 km.

whole air parcel is transported horizontally and vertically with all its major and minor constituents. This is in contrast with 1-D models which need eddy diffusion to attempt to reproduce the Martian NO emission [Cox *et al.*, 2008, 2010], and NO and O<sub>2</sub> Venusian emission [Gérard *et al.*, 2009a]. In this 1D scheme, there is no vertical transport of CO<sub>2</sub>; the O and N atoms are “percolating” downward through the CO<sub>2</sub>. In such a case, the downward vertical flux of CO<sub>2</sub> associated with the observed O<sub>2</sub> emission is zero, by definition. On the contrary, with the 3-D simulation, such an atmospheric flux can be calculated, allowing an estimate of the average residence time of one single molecule at all altitudes, and corresponding photochemical lifetime, since the photodissociation rate depends very much on the altitude.

[25] Detailed results from the GCM are beyond the scope of the present paper. However, one may do the following exercise. Taking one vertical profile of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emissivity at a particular place and season, one may consider an equivalent stationary 1D model, in which a constant downward advection flux at 70 km (above the emitting layer) takes place with a constant mixing ratio of O/CO<sub>2</sub>. The OMEGA observed (vertical) emission rate of 0.24 MR corresponds to the recombination of  $2 \times 0.24 \times 10^{12}/0.75 = 6.4 \times 10^{11}$  O atoms/s in a column of 1 cm<sup>2</sup>. The factor of 0.75 is the net effective quantum yield for the production of

O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) from reaction (1). We neglect the loss of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) by quenching with CO<sub>2</sub> molecules, which is justified at the altitude of the nightglow observed by OMEGA. In this stationary picture, the recombination of O atoms in the column must be replaced by fresh atoms at 70 km by an equivalent downward flux. The density of O atoms at this altitude is  $1.8 \times 10^{11}$  cm<sup>-3</sup> in the GCM, which calls for a vertical descent velocity of 3.5 cm/s.

[26] Given that the model mixing ratio O/CO<sub>2</sub> is  $5 \times 10^{-3}$  at 70 km, one may compute a downward flux of CO<sub>2</sub>, and a fluence over one year of  $4 \times 10^{21}$  molecules/cm<sup>2</sup>. The whole column of air would be replaced in 44 years. If a molecule, like CH<sub>4</sub>, is destroyed rapidly at altitudes above 70 km, then we may assume that the air coming down would be devoid of CH<sub>4</sub>, and the actual lifetime would be 44 years, instead of  $\sim 300$  for the photochemical lifetime at ground level. However, this computation could apply to the whole planet only if the intensity observed by OMEGA would be seen permanently and everywhere, which is by far not the case (Figure 2). Therefore, recycling of the atmosphere at high altitude seems far too slow to significantly decrease the low altitude lifetime of CH<sub>4</sub>.

#### 4. Conclusions

[27] We report the first detection in the atmosphere of Mars of the nightside O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission at 1.27  $\mu$ m from observations of the OMEGA imaging spectrometer on board Mars Express, demonstrating a new remote-sensing diagnosis of the aeronomy and atmospheric dynamics of Mars. These observations provide strong constraints on the latitude-season behavior of the downward transport of CO<sub>2</sub> and trace species from the thermosphere on Mars. The observed vertical intensity can be transformed into a downward advection velocity, found to be 3.5 cm/s at 70 km, at the time and place of strong emissions.

[28] Data were compared to the output of a general circulation model with photochemistry. The overall agreement is good, in particular in the latitude/season distribution of the emission. The observed intensities are slightly lower than the predicted ones, but with only three examples of detection, it would be premature to draw a definitive conclusion on this aspect. The most significant departures are on the thickness of the layer (thicker in the model) and the peak altitude, higher in the model.

[29] We have investigated briefly if the vertical circulation implied by the reported O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) nighttime emission is sufficient to decrease significantly the lifetime of CH<sub>4</sub> through exposure to UV at high altitudes. A rough calculation indicates that, if the reported emissions were ubiquitous and permanent on the nightside, it would shorten the average lifetime to 44 years. However, both the OMEGA observations and the GCM model show that the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) emission is confined to winter polar regions only (Figure 2). Therefore, recycling of the atmosphere through high altitude regions seems quite insufficient to reconcile methane observations and modeling.

[30] These observations of OMEGA on Mars Express pave the way for further studies of general circulation with the IR channel of SPICAM (with a better spectral resolution, but poorer sensitivity and spatial resolution, 1° FOV (A. A. Fedorova *et al.*, The O<sub>2</sub> nightglow in the Martian

atmosphere by SPICAM onboard of Mars-Express, submitted to *Icarus*, 2011)), and also with the CRISM spectrometer on board the Mars Reconnaissance Orbiter which reported similar O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ) nightglow emission [Clancy *et al.*, 2010]. In particular, if both O<sub>2</sub> and NO emission could be observed at the same time and same location, the use of the model could check the overall consistencies of the results, and perhaps determine the rate constant for reaction (1) at the low temperatures of Mars polar night. The atmosphere of Mars would be used as a gigantic laboratory to perform a measurement of a rate constant.

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