



# Seasonal Changes in the Vertical Structure of Ozone in the Martian Lower Atmosphere and Its Relationship to Water Vapor

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## Special Section:

ExoMars Trace Gas Orbiter -  
One Martian Year of Science

## Key Points:

- Observations of the vertical distribution of ozone on Mars over 3 years
- Direct comparison of water vapor, ozone, and temperature, revealing trends and correlations
- Ozone is observed in higher abundances than photochemical models predict

## Supporting Information:

Supporting Information may be found in the online version of this article.

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



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## Seasonal Changes in the Vertical Structure of Ozone in the Martian Lower Atmosphere and Its Relationship to Water Vapor

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**Abstract** The mid-infrared channel of the Atmospheric Chemistry Suite (ACS MIR) onboard the ExoMars Trace Gas Orbiter is capable of observing the infrared absorption of ozone (O<sub>3</sub>) in the atmosphere of Mars. During solar occultations, the 003←000 band (3,000–3,060 cm<sup>−1</sup>) is observed with spectral sampling of ~0.045 cm<sup>−1</sup>. Around the equinoxes in both hemispheres and over the southern winters, we regularly observe around 200–500 ppbv of O<sub>3</sub> below 30 km. The warm southern summers, near perihelion, produce enough atmospheric moisture that O<sub>3</sub> is not detectable at all, and observations are rare even at high northern latitudes. During the northern summers, water vapor is restricted to below 10 km, and an O<sub>3</sub> layer (100–300 ppbv) is visible between 20 and 30 km. At this same time, the aphelion cloud belt forms, condensing water vapor and allowing O<sub>3</sub> to build up between 30 and 40 km. A comparison to vertical profiles of water vapor and temperature in each season reveals that water vapor abundance is controlled by atmospheric temperature, and H<sub>2</sub>O and O<sub>3</sub> are anti-correlated as expected. When the atmosphere cools, over time or over altitude, water vapor condenses (observed as a reduction in its mixing ratio) and the production of odd hydrogen species is reduced, which allows O<sub>3</sub> to build up. Conversely, warmer temperatures lead to water vapor enhancements and ozone loss. The LMD Mars Global Climate Model is able to reproduce vertical structure and seasonal changes of temperature, H<sub>2</sub>O, and O<sub>3</sub> that we observe. However, the observed O<sub>3</sub> abundance is larger by factors between 2 and 6, indicating important differences in the rate of odd-hydrogen photochemistry.

**Plain Language Summary** Ozone on Mars is part of the so-called odd-oxygen family of reactive, oxidizing gases. It is part of many chemical cycles that help convert one type of gas into another, facilitating the transfer of carbon or hydrogen. Odd-oxygen is crucial to linking the cycles of water vapor and carbon dioxide, or the destruction of trace gases, such as methane. With the Atmospheric Chemistry Suite onboard the ExoMars Trace Gas Orbiter, we are able to study the vertical structure of ozone in the Martian atmosphere and make direct comparisons between it and water vapor and temperature. We have observed ozone abundances several times larger than predicted, suggesting that the oxidizing power of the Martian atmosphere is stronger or faster than expected. We have also observed and measured the relationship between these products: temperature controls the abundance of water vapor, and when the atmosphere cools and water condenses, ozone is able to build up. It is the by-products of when water vapor breaks down in sunlight that remove odd-oxygen from the atmosphere.

## 1. Introduction

Ozone (O<sub>3</sub>) plays a crucial role in the atmospheric chemistry of Mars. O<sub>3</sub> was first observed by the Ultraviolet Spectrometers on Mariner 7 and 9 (Barth & Hord, 1971; Barth et al., 1973), instruments on Mars Express and the ExoMars Trace Gas Orbiter (TGO) have been able to investigate its relationship with water vapor (Lefèvre et al., 2021), its vertical structure (Khayat et al., 2021; Olsen et al., 2020), and its seasonal evolution (Patel et al., 2021). Ozone is produced via the photolysis of carbon dioxide (CO<sub>2</sub>) and subsequent reactive combination of molecular and atomic oxygen. O<sub>3</sub> is disassociated by photolysis, but this pathway does not yield a net change

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in odd-oxygen (O and O<sub>3</sub>) species. Destruction of odd-oxygen most frequently occurs when atomic oxygen reacts with the hydroperoxyl radical (HO<sub>2</sub>), a member of the odd-hydrogen family (with H and OH).

Odd-hydrogen molecules are primarily derived from water vapor photolysis and are responsible for stabilizing the ratio of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). A long standing problem in Martian photochemical modeling is that over long time scales the amount of CO is underestimated (Lefèvre & Krasnopolsky, 2017). The reaction between hydroxyl (OH) and CO maintains the CO<sub>2</sub> mixing ratio of 95.6%. HO<sub>2</sub> and OH are very difficult to observe directly, but their coupling to water vapor (H<sub>2</sub>O), which is their source molecule, and with ozone, as the odd-oxygen loss mechanism, allows the monitoring of ozone to be used as a proxy for odd-hydrogen species. Going further, a comparative study of water vapor and ozone can shed insight into several aspects of Martian photochemistry since their changing relative abundance reflect the rates of change of odd-oxygen and odd-hydrogen, which in turn control other Martian atmospheric constituents such as CO, CO<sub>2</sub>, HCl, or nitrogen species.

The integrated column abundance of O<sub>3</sub> has been revealed over broad spatial areas and temporal scales by observations from the Earth (Esenak et al., 1991; Fast et al., 2006), the Hubble Space Telescope (Clancy, Wolff, et al., 1996), and by the Mars Color Imager (MARCI) onboard the Mars Reconnaissance Orbiter (Clancy et al., 2016). SPICAM (SPectroscopie pour l'Investigation des Caractéristiques Atmosphériques de Mars) on Mars Express has been able to produce both vertical profiles and column abundances of O<sub>3</sub> (Lefèvre et al., 2021; Montmessin & Lefèvre, 2013; Perrier et al., 2006). The Ultraviolet and Visible Spectrometer (UVIS) channel of the Nadir and Occultation for Mars Discovery (NOMAD) instrument on TGO has been able to create a high density data set of O<sub>3</sub> number density vertical profiles with fine resolution (Khayat et al., 2021; Patel et al., 2021). These studies have confirmed the expected anti-correlation with water vapor, revealed a strong increase in ozone abundance over the poles during winters, and seasonality characterized by higher ozone abundances reaching to higher altitudes during the aphelion period.

The mid-infrared channel of the Atmospheric Chemistry Suite (ACS MIR) makes fine spectral resolution (separation of ~0.045 cm<sup>-1</sup>) solar occultation measurements from the near-polar, circular orbit of TGO. This technique has been shown to be sensitive enough to observe the infrared absorption lines of the 003←000 absorption band of O<sub>3</sub> below 40 km. From the same ACS MIR observations, we can also derive coincident mixing ratios of water vapor. The near-infrared channel (ACS NIR) makes simultaneous observations of the same air mass, and provides coincident measurements of temperature and pressure. Herein, we investigate the vertical structure of O<sub>3</sub> revealed by ACS MIR and make direct comparisons with simultaneously measured vertical profiles of water vapor abundance and temperature. In the following sections we will introduce the instrument and analysis methods, present the vertical profiles of O<sub>3</sub>, H<sub>2</sub>O, and temperature, organized by season and latitude range, compare these results to data from the LMD Mars Global Climate Model (GCM), and discuss the quantized relationship between H<sub>2</sub>O and O<sub>3</sub>.

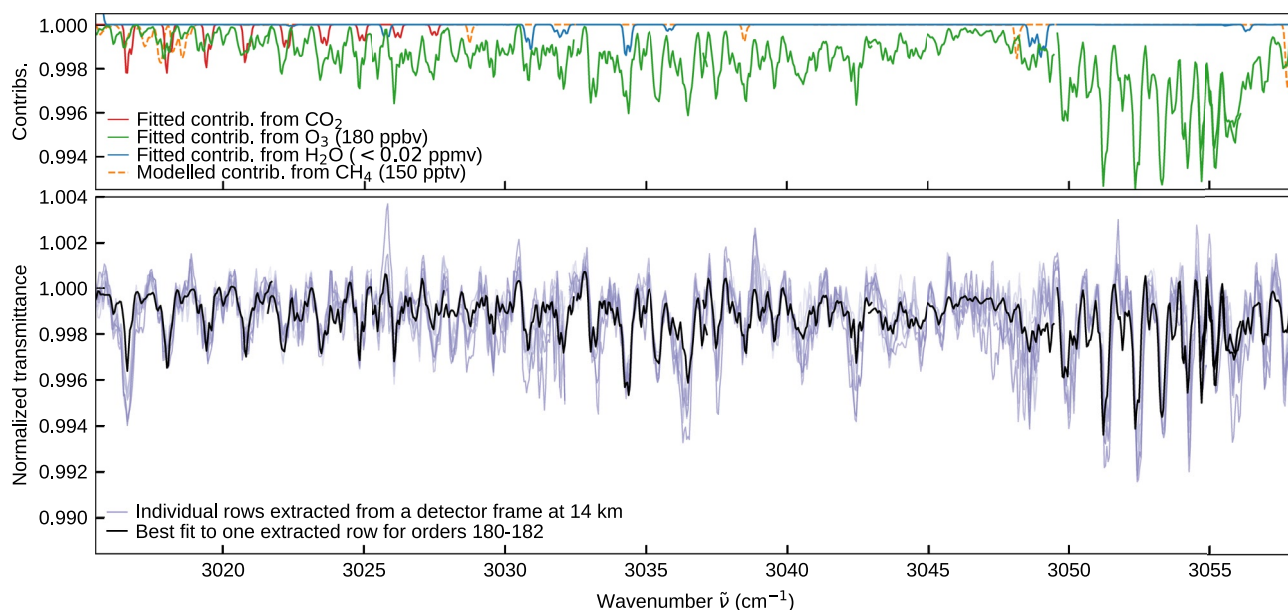
## 2. Materials and Methods

### 2.1. ACS MIR

The ExoMars Trace Gas Orbiter entered Martian orbit in late 2016, and commenced its nominal science phase in April 2018, midway through Mars year (MY) 34, and just before a global storm began as Mars approached perihelion, and summer began in the southern hemisphere. It carries four scientific instruments: a stereo camera, a neutron detector, and two spectrometer suites to study the composition of the atmosphere. The Atmospheric Chemistry Suite consists of an electronics block and three instrument channels investigating: the thermal infrared (ACS TIRVIM), the near-infrared (ACS NIR), and the mid-infrared (ACS MIR).

ACS MIR is a cross-dispersion spectrometer consisting of a large echelle diffraction grating that provides access to the infrared spectral range, coupled to a secondary diffraction grating that separates the high diffraction orders (Korablev et al., 2018). The secondary grating is steerable, and each position provides access to a specific instantaneous spectral range. The secondary grating position used in this study is 12, which allows us to observe diffraction orders 173–192 covering the spectral range 2,850–3,250 cm<sup>-1</sup>. This position contains the spectral features of O<sub>3</sub>, HCl, H<sub>2</sub>O, and CO<sub>2</sub>, and is used in the search for CH<sub>4</sub>.

ACS MIR operates in solar occultation mode, making a series of observations of the sun while the atmosphere is between the sun and the spacecraft. Each observation in an occultation sequence is at a unique tangent height,



**Figure 1.** Example atmospheric chemistry suite mid-infrared (AIC MIR) spectra showing ozone absorption features. The top panel shows contributions to the best-fit line for different gases. The *P* and *R* branches of the  $003 \leftarrow 000$  vibration rotation band of  $O_3$  are distinct and dominate the spectral range. Water vapor lines are not present and a portion of the newly identified magnetic dipole band of  $CO_2$  is visible at lower wavenumbers. Also indicated are the locations of  $CH_4$  absorption lines that are targeted in this configuration of ACS MIR. The lower panel shows normalized spectra from orders 180–182 extracted from 11 rows of the ACS MIR detector images (shades of purple) and a best-fit line for one row (black). Each row corresponds to a unique tangent height, separated by  $\sim 175$  m.

providing a vertical resolution of 1–4 km, depending on the orbital geometry. Spectra are recorded on a two-dimensional detector, over which the *x*-axis corresponds to wavenumber and the *y*-axis separates the diffraction orders. Each diffraction order appears as a stripe over the detector covering around 20 rows. The width of the stripe corresponds to the vertical field of view of the instrument, so each row is a unique transmission spectrum separated by  $\sim 100$ – $200$  m (Korablev et al., 2018; Olsen, Lefèvre, et al., 2021; Trokhimovskiy et al., 2020).

The entire sequence of solar occultation observations (one extracted spectrum at each tangent height) is analyzed at once to obtain vertical profiles of the target quantities. Observations made above the top of the atmosphere provide a measurement of the solar spectrum, which is used for radiance calibration and to convert solar emission spectra into atmospheric transmission spectra. Example spectra are shown in Figure 1 over the spectral region containing the absorption band of ozone (at wavenumbers where no sunlight is absorbed, the transmission spectra are unity).

## 2.2. Retrievals

Vertical profiles of the volume mixing ratio (VMR) of target gases are made using the JPL Gas Fitting Software (GFIT or GGG; Irion et al., 2002; Wunch et al., 2011). At each tangent height (defined relative to the aeroid) and over a specified spectral fitting window, a forward model is computed using volume absorption coefficients derived from the 2020 edition of the HITRAN database (Gordon et al., 2021), a priori VMR profiles for various gases, vertical profiles of temperature and pressure, and computed optical path through the atmosphere. Where available, line shape parameters for broadening in a  $CO_2$ -rich atmosphere are used (Devi et al., 2017; Gamache et al., 2016; Tudorie et al., 2012; Wilzewski et al., 2016). Spectral fitting is performed using non-linear Levenberg-Marquardt minimization in which target gas VMR profiles are varied to obtain the best-fit. Temperature and pressure data are obtained from simultaneous measurements made using the ACS NIR instrument (Fedorova et al., 2020, 2022), which observes strong  $CO_2$  bands upwards of 90 km. *A priori* VMRs of major gases ( $CO_2$ ,  $H_2O$ ,  $O_3$ ) were extracted from the LMD GCM with photochemistry (Lefèvre et al., 2004, 2021) at the local times of the solar terminator for the latitudes and solar longitudes ( $L_s$ ) of ACS occultations. A set of estimated slant column abundances for all observed tangent altitudes is inverted with calculated slant column paths traced through the atmosphere using a linear equation solver to obtain a retrieved VMR vertical profile. This approach

to solar occultation limb observations accounts for each atmospheric layer with decreasing number density along the optical path from the tangent point. This approach was previously used to study CO, O<sub>3</sub> and HCl with ACS MIR (Korablev et al., 2021; Olsen et al., 2020; Olsen, Lefèvre, et al., 2021).

Several studies have been performed using ACS MIR data where a single spectrum close to the edge of the observational slit nearest the center of the Sun was analyzed at each tangent height (e.g., Alday et al., 2019; Korablev et al., 2019; Olsen et al., 2020; Trokhimovskiy et al., 2020), which is very computationally efficient. To improve the sensitivity of ACS MIR when absorption feature depths approach the noise level of a spectrum, such as when studying gases present in only trace amounts, or at higher altitudes, more data from the detector frame can be used. This method was developed to improve the retrievals of the trace gas hydrogen chloride (HCl) (Olsen, Trokhimovskiy, Montabone, et al., 2021), and was used to determine upper limits for phosphine (Olsen, Trokhimovskiy, Braude, et al., 2021). This also helps to mitigate complications arising from a changing instrument line shape (ILS; Olsen, Lefèvre, et al., 2021). There is an optical aberration in the imaging subsystem that can cause absorption lines to appear as a double image, the relative magnitude of which changes across the detector frame and vertical field of view. If the ILS is fitted, temperatures, densities and VMRs can be accurately retrieved from such spectra (Alday et al., 2019; Belyaev et al., 2021; Olsen, Lefèvre, et al., 2021).

Each diffraction order is represented by a stripe across the detector array and upwards of 11 rows can be extracted and analyzed. Each row is a unique transmission spectrum with its own tangent height (separated by only 0.1–0.2 km), line depths, noise level, and ILS. Examples of 11 spectra extracted from one frame are shown in Figure 1. Sets of occultation spectra are made by grouping the spectra by row (a set of all the top-most spectra, a set of the second row, etc.), since these should have similar noise levels and ILSs, and VMR vertical profile retrievals are performed on each set. The weighted average of the profiles is taken to be the best estimate of the vertical profile of the target gas VMR, and it is assigned the standard deviation of the weighted mean as an uncertainty. This method has been shown to significantly improve the accuracy of a retrieval (Olsen, Trokhimovskiy, Montabone, et al., 2021), since the impact of any data quality issues for a single spectrum are reduced (spurious features, inaccuracies when measuring quantities such as the solar spectrum, corrupted data, interpolation errors, etc.). Validation of ACS MIR data is frequently done by making comparisons of water vapor retrievals to those from ACS NIR (Fedorova et al., 2020), and this method, applied to secondary grating positions 11 and 12, has improved the stability of the ACS MIR retrievals, their accuracy, and their agreement with ACS NIR. It is used for both water vapor and ozone retrievals presented here.

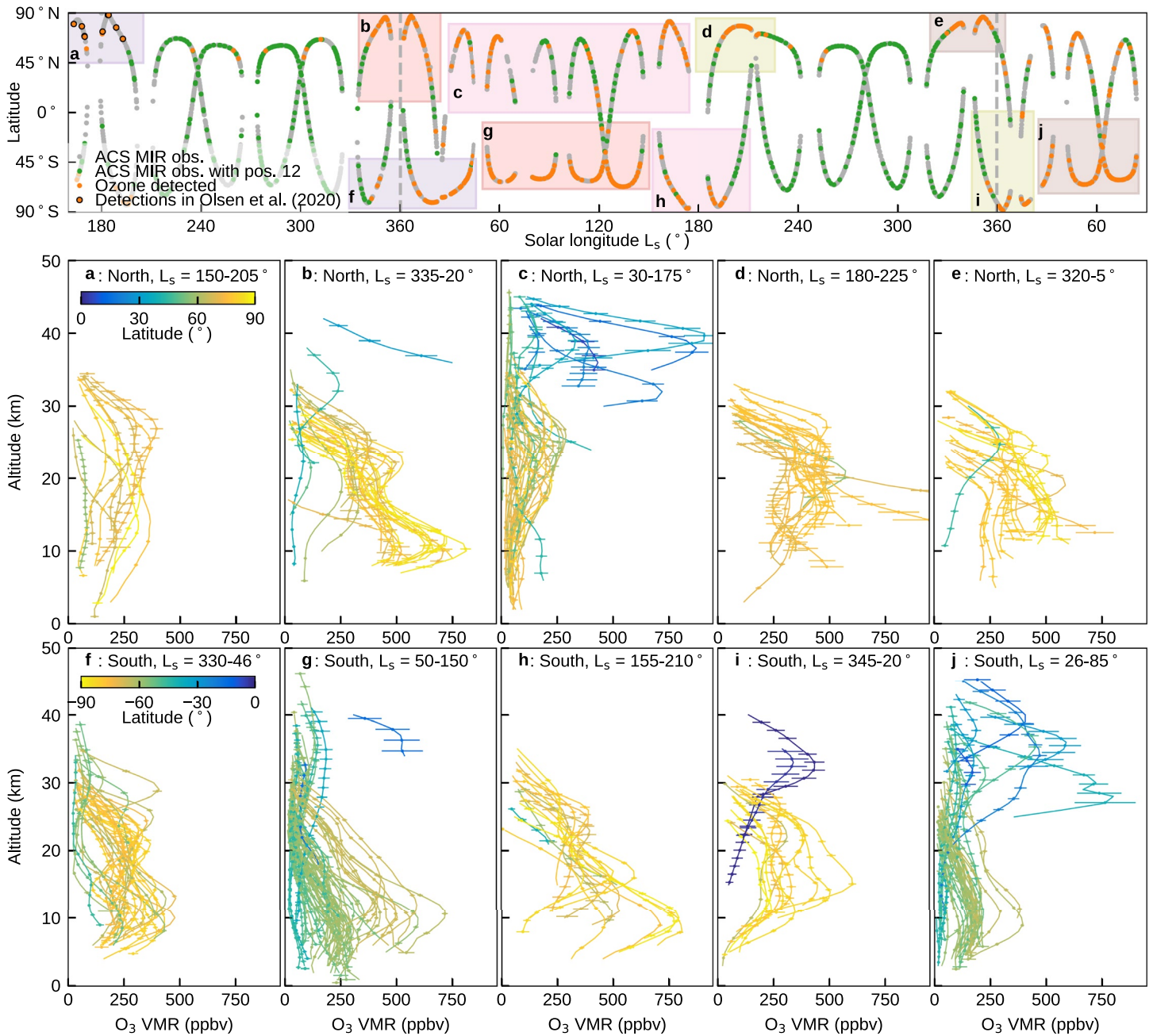
### 3. Observations of O<sub>3</sub> With ACS MIR

The TGO entered Mars orbit in the fall of 2016 and began nominal science operation in April 2018 after an aerobraking campaign to circularize its near-polar orbit. Data taking with ACS MIR began on L<sub>s</sub> 163° of MY 34 and has continued through the end of MY 35 and continues in MY 36. Opportunities for solar occultation measurements occur twice per orbit, and secondary grating position 12 is used about 15% of the time.

Figure 2 provides an overview of the ACS MIR O<sub>3</sub> observations (349 vertical profiles). The top panel shows the latitudes of observations as a function of solar longitude. The poleward extent of the observations depends on the angle of the plane of Mars' axial tilt and the sun. This is maximum at the equinoxes when they are perpendicular, and minimum between, when they are aligned and the poles experience polar day or night (which cannot be observed in solar occultation). Ozone is regularly detected toward the poles, as indicated in Figure 2 (top panel), during the equinoxes and during the winters in both hemispheres when its abundance should be highest due to the cold and dry atmospheric conditions. It is never detected during southern summer due to the wet atmosphere, but is observed in northern summer, which is drier and cooler above 10 km relative to summer in the south.

The lower panels of Figure 2 show the individual retrieved vertical profiles of O<sub>3</sub> VMR. Profiles are grouped by L<sub>s</sub> in each panel, and the L<sub>s</sub> bounds are indicated in the top panel. The L<sub>s</sub> range used for each grouping is based partially on season, but also on the trajectory of the latitudes of observations over time, shown in the top panel. There are four key pieces of information that can be derived from these observations, and they are explored in the following sections, in which we compare O<sub>3</sub> VMRs to retrieved water vapor abundances and temperatures. The first is that O<sub>3</sub> is very difficult to detect during almost the entire perihelion period between the autumnal and vernal equinoxes (L<sub>s</sub> = 220–240°), during which the atmosphere is warm, dusty, and moist in both hemispheres due to the southern summer. Detections in the northern hemisphere are rare, and ozone is not seen in the southern





**Figure 2.** Overview of ozone detections with atmospheric chemistry suite mid-infrared (ACS MIR). The top panel shows the distribution of latitudes probed by ACS over time (solar longitude  $L_s$ ) since the start of the mission on  $L_s$  163° in Mars year (MY) 34 through to the end of MY 35 and into the beginning of MY 36. All ACS occultations are indicated in gray, those using secondary grating position 12 green, and those with  $3\sigma$  ozone detections are highlighted in orange. Positive detections are grouped by  $L_s$  and latitude, and the retrieved vertical profiles are shown in the lower panels. Panels a–e cover the northern hemisphere, and panels f–j cover the southern hemisphere.

hemisphere. In contrast, O<sub>3</sub> is plentiful at all latitudes in the southern hemisphere during the aphelion period, when it is winter in the south (Figure 2g). Third, ozone is most plentiful at high latitudes between seasons (yellow profiles in panels b, d, e, f, h, and i of Figure 2), and finally, an ozone layer near 40 km appears toward the equator during the aphelion period (blue profiles in panels b, c, d, i, and j in Figure 2). Figure 2 is reproduced in Figure S2 in Supporting Information S1 using O<sub>3</sub> data computed with the LMD Mars General Circulation Model (GCM), which is discussed in Section 5 (note that GCM data is only available up to the end of MY 35).

It is expected that there is great variation in  $O_3$  VMRs between day and night, when  $O_3$  photolysis is arrested, and TGO observations are made at either dawn or dusk. However, these diurnal changes are not evident in our data set since over any  $L_s$  period, comparing morning and evening observations necessitates a change in hemisphere as well. Local times as a function of  $L_s$  are shown in Figure S1 in Supporting Information S1. To compare observations made at a morning terminator with those made in the evening, and remaining within the same latitude is generally only possible with observations separated by  $10\text{--}20^\circ$  of  $L_s$  (20–40 days). Changes observed between evening and morning data must be also considered in terms of changes in latitude and  $L_s$  as well, which are much more prominent (note that at lower latitudes where the  $L_s$  spacing gets closer, have the higher changes in latitude over time as well).

The data in Figure 2a include the initial results reported by Olsen et al. (2020) but reproduced here after three major changes to the analysis method: the results are the mean of analyzing 11 spectra; improved estimation of the background signal intensity; and the temperature and pressure used were updated (Fedorova et al., 2020). The shapes of the profiles remain very similar to those published previously in Olsen et al. (2020), but with reduced uncertainties and an extension upwards from 30 to 35 km. The magnitudes of the profiles have changed, but not uniformly, and the approximate  $O_3$  VMR remains around 200 ppbv. Increases in  $O_3$  VMR on the order of 25% are seen after the improvements to the retrievals and data processing. Differences are due to changes in the spectral processing (especially background light calculation) and retrieval algorithm (including the retrievals from multiple rows of the detector frame).

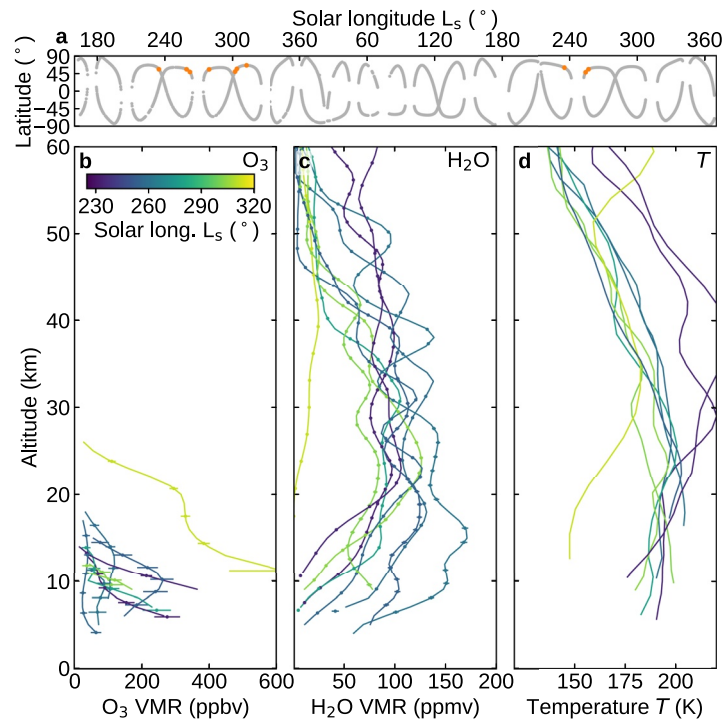
In the following section, we present coincident vertical profiles of  $O_3$  VMR,  $H_2O$  VMR, and temperature. We examine first the observations made during the aphelion period at high northern latitudes, then those during the aphelion period at far southern latitudes and high northern latitudes. The transitory periods around the equinoxes and the lower middle to equatorial aphelion observations are also presented. The  $L_s$  bounds between these groupings are based on both the shapes and magnitudes of the water vapor and ozone vertical profiles, so chosen to be climatologically similar, as well as the boundaries applied by the periodic changes in solar occultation latitude over  $L_s$ .

#### 4. $O_3$ Chemistry in the Martian Atmosphere

The Martian atmosphere is characterized in terms of seasons similarly to Earth due to its axial tilt. For example, the northern summer solstice occurs on  $L_s$   $90^\circ$ . Such seasonality is especially visible in nadir observations of its atmosphere, which have provided the dominant view of contemporary Martian climate (e.g., Clancy, Grossman, et al., 1996; Perrier et al., 2006; Smith, 2004). This includes observations of  $O_3$  which reveal enhancement toward the poles in winters (Perrier et al., 2006). However, nadir observations are sensitive to the lower layers of the atmosphere, and this picture is for altitudes greater than 10 km. Seasonal cycles of temperature and water vapor at altitudes probed by ACS are instead controlled by the orbital eccentricity of Mars, which is much larger than Earth's, revealing north-south symmetries in seasonal cycles (e.g., Aoki et al., 2019; Fedorova et al., 2020).

During the time period surrounding aphelion ( $L_s = 71^\circ$ ), in which it is approaching summer in the northern hemisphere and winter in the south, warming near the surface over the northern pole leads to the formation of a water vapor layer, but is restricted to below 20 km (Alday et al., 2021). Deep winter cooling over the south pole regions causes condensation of both  $CO_2$  and water vapor on the surface. Conversely, the Martian climate in the period surrounding perihelion is driven by the spring-time sublimation of the southern seasonal ice cap and is characterized by increased atmospheric density, the lifting of dust into the atmosphere, and increased warming of the atmosphere and elevation of the hygropause. Outside regions of polar night or polar day, these effects are global, leading to an atmosphere from 5 to 60 km that is wetter and warmer during winter than the summer in the northern hemisphere (Alday et al., 2019; Aoki et al., 2019; Fedorova et al., 2020).

ACS MIR observations of  $O_3$  during the perihelion result in very few  $O_3$  detections, with upper limits of  $\sim 5\text{--}10$  ppbv between 10 and 40 km. In the south during the spring and summer,  $O_3$  is not detected, and in the north during fall and winter it is rarely detected; and when so, it is almost always in the presence of water vapor. Figure 3 shows the coincident retrieved vertical profiles (above the areoid) measured during the northern winters around perihelion of  $O_3$  VMR from ACS MIR,  $H_2O$  VMR from ACS MIR, and temperature from ACS NIR (note ACS NIR data is only available up to the start of MY 36). This novel comparison of coincident data set, along



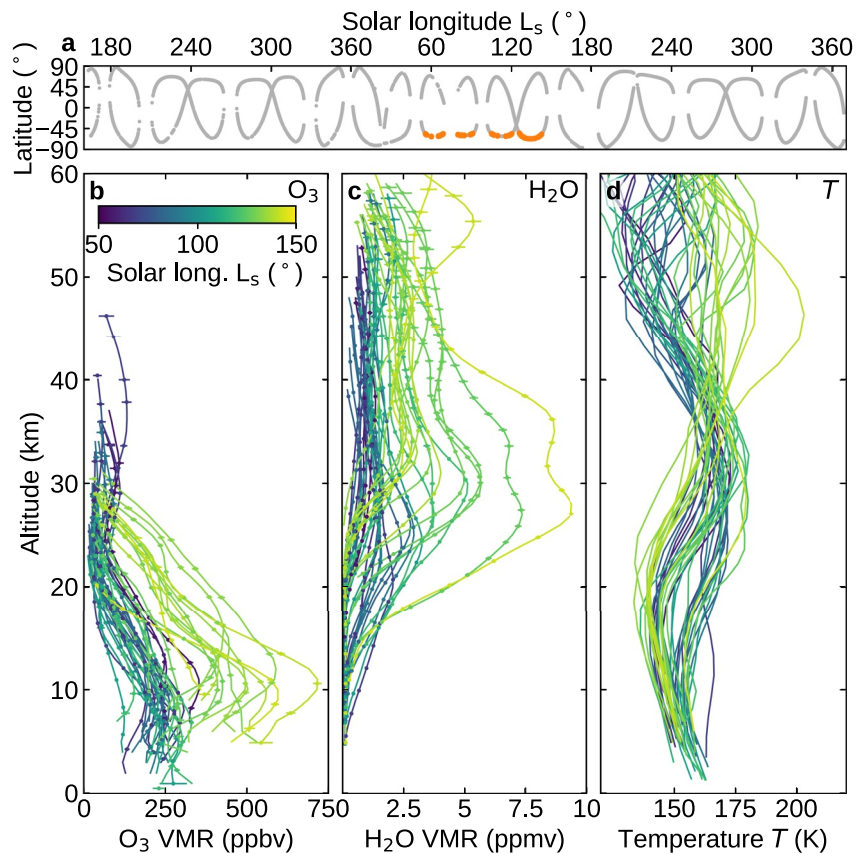
**Figure 3.** Perihelion ozone observations during northern fall and winter. Panel a shows the latitude and  $L_s$  of observations, retrieved volume mixing ratio vertical profiles of ozone (panel b) and water vapor (panel c) retrieved from atmospheric chemistry suite mid-infrared (ACS MIR), and temperature retrieved from ACS near-infrared channel (panel d). Colors indicate  $L_s$ . These profiles were measured at middle northern latitudes ( $47^\circ\text{N}$ – $66^\circ\text{N}$ ) around the perihelion period (northern winter).

the vertical follows a direct comparison of ozone and water vapor column abundances measured with SPICAM (Lefèvre et al., 2021).

Water vapor is present at VMRs  $> 100$  ppmv above 10 km, but, as these measurements are made toward polar latitudes (but south of  $60^\circ\text{N}$ ) there is a cold layer below 15 km (Fedorova et al., 2020) causing water to condense and the VMRs to be rapidly reduced below 20 km. This allows ACS to occasionally observe a near-polar ozone layer toward the surface with VMRs between 50 and 200 ppbv. A polar ozone layer over the surface is expected (Clancy et al., 2016; Perrier et al., 2006), but the lack of detected  $O_3$  in most observations and the presence of  $H_2O$  suggests ACS MIR occultations are generally outside the polar vortex, which may extend south to  $60^\circ\text{N}$  (e.g., Mitchell et al., 2015; Waugh et al., 2016). Most of these observations occur at  $55^\circ\text{N}$ . The polar vortex is not expected to be symmetric and may be sampled irregularly by ACS MIR, depending on  $L_s$  and longitude. A notable exception occurred at  $L_s = 312^\circ$  and  $66^\circ\text{N}$ . This observation reveals a substantially colder atmosphere below 30 km, with very low water vapor, resulting in 200 ppbv  $O_3$  up to 25 km. NOMAD observations in the UV during the time period tend to be restricted to above 20 or 30 km, but reveal a measurable low number density at the lower altitude limits of their observations, and very low abundances above (Patel et al., 2021).

Southern winter observations made during the aphelion period (panel g in Figure 2) are shown in Figure 4, which presents vertical profiles of temperature and the VMRs of  $O_3$  and  $H_2O$ . These profiles were recorded in the southern hemisphere at latitudes between  $55^\circ\text{S}$  and  $66^\circ\text{S}$ . In sharp contrast to the northern winter, atmospheric temperatures below 20 km are  $< 150$  K and only rise to 165 K around 30 km. The colder aphelion atmosphere results in much lower VMRs of water vapor by almost an order of magnitude and less than 1.5 ppmv below 20 km. At these latitudes, this allows ozone to remain in the atmosphere below 20 km. While ACS MIR solar occultations do not probe the polar nights during winters, the observed  $O_3$  is likely associated with polar vortex activity, which is expected to be weaker during the southern winters than those in the north, but cover a much broader extent, reaching north of  $50^\circ\text{S}$  (Waugh et al., 2016). NOMAD observations from this time and latitude range reveal the highest observed  $O_3$  number densities below 20 km (Patel et al., 2021).



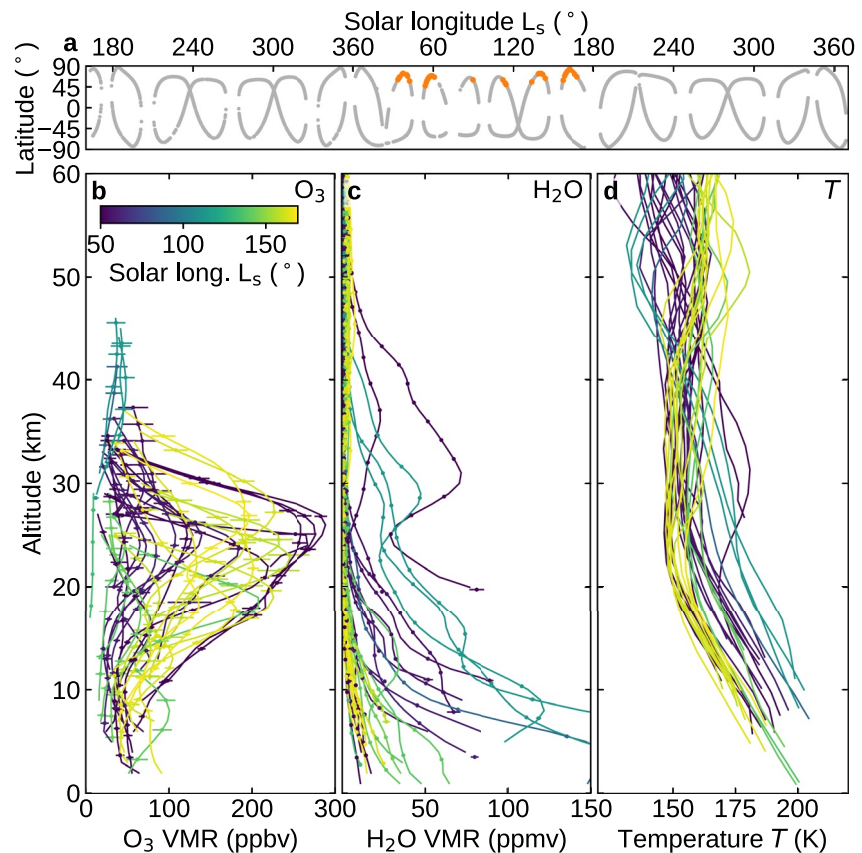


**Figure 4.** Aphelion ozone observations during southern winter. Panel a shows the latitude and  $L_s$  of observations, volume mixing ratio vertical profiles of ozone (panel b) and water vapor (panel c) retrieved from atmospheric chemistry suite mid-infrared (ACS MIR), and temperature retrieved from ACS near-infrared channel (panel d). Colors indicate  $L_s$ . These profiles were measured at middle southern latitudes (55°S–66°S) during the aphelion period (southern winter) and correspond to Figure 2g.

We observe around 200 ppbv O<sub>3</sub> in the lowest layers of the atmosphere, from 15 km to the surface, before  $L_s = 120^\circ$ . O<sub>3</sub> decreases toward 20 km, to undetectable levels above 30 km, consistent with observed increases in H<sub>2</sub>O VMR from 1 to 5 ppmv at those altitudes. The O<sub>3</sub> enhancement seen at 30 km occurs during a time period in which Montmessin and Lefèvre (2013) reported a layer of O<sub>3</sub> over the south polar region (70°S–80°S) and attributed it to poleward transport of oxygen. Our observations are restricted to higher latitudes, and those early profiles in Figure 4b are the northern-most in this data set (toward to 55°S) and more likely related to aphelion cloud belt formation (discussed below).

A portion of the O<sub>3</sub> profiles shown in Figure 4b have consistently higher VMRs (brighter green to yellow colors). These are from the latest  $L_s$  period in this grouping and were generally recorded at further southern latitudes (brighter yellow colors in Figure 2g also). To show this, Figure 4 is reproduced as Figure S3 in Supporting Information S1 with the profiles colored by latitude. For these highest latitude southern winter profiles, we observe also the coldest temperatures in the lower atmosphere, combined with warmer temperatures above 30 km. This results in the largest H<sub>2</sub>O VMRs above 30 km, but also peak H<sub>2</sub>O VMR gradient and nearly no detectable water vapor below 25 km, leading to higher ozone abundances at these lower altitudes.

Stellar occultation and nadir observations made by SPICAM have been able to show that there are unique mechanisms impacting ozone abundance over the poles during the winter polar nights. SPICAM O<sub>3</sub> vertical profiles during the southern polar winter were compared with GCM simulations to show that transport of high-altitude oxygen-rich air from sunlight regions leads to an ozone layer forming at 50 km (Montmessin & Lefèvre, 2013). Integrated column abundances, combined with GCM simulations, have shown that H<sub>2</sub>O photolysis is no longer responsible for O<sub>3</sub> destruction near the surface (Lefèvre et al., 2021) poleward of  $\pm 60^\circ$ . ACS MIR solar

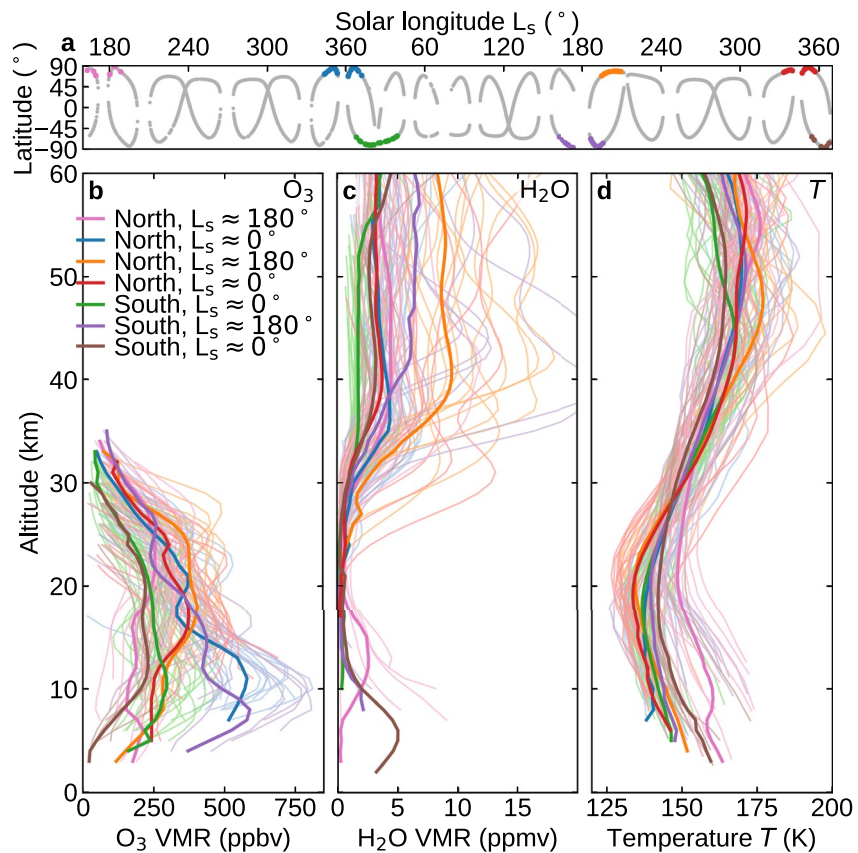


**Figure 5.** Aphelion ozone observations during northern late spring and summer. Panel a shows the latitude and  $L_s$  of observations, volume mixing ratio vertical profiles of ozone (panel b) and water vapor (panel c) retrieved from atmospheric chemistry suite mid-infrared (ACS) MIR, and temperature retrieved from ACS near-infrared channel (panel d). Colors indicate  $L_s$ . These profiles were measured at northern latitudes (55°N–66°N) during the aphelion period (northern summer) and correspond to Figure 2c.

occultations during the perihelion period covering northern winter are not able to verify these mechanisms, however, since they are restricted further south, to the sunlight regions of Mars.

During the same  $L_s$  period, but in the northern hemisphere, we observed similarly cold temperatures around 20–30 km, resulting in low water vapor abundances and peak ozone abundances. These profiles are shown in Figure 5 and correspond to Figure 2c. In contrast to the south, the lower atmosphere has warmed, associated with northern summer, such that water vapor increases near the surface, and ozone is depleted below 20 km. The number densities reported by Patel et al. (2021) do not reveal a decrease in O<sub>3</sub> abundance and observe a more uniform O<sub>3</sub> density up to 50 km. Most ACS observations in which ozone was observed occurred closer to the equinoxes, which was also observed with NOMAD. Observations with maximum O<sub>3</sub> values over this  $L_s$  period correspond to the spring (dark blue profiles) and fall (yellow profiles) boundaries of the northern summer solstice. Summer solstice O<sub>3</sub> values (green-blue profiles) are very low since the atmosphere is sufficiently warm during the middle of this  $L_s$  period to host water vapor, leading to ozone depletion.

TGO solar occultation opportunities probe the furthest toward the poles during the equinoxes when the plane of Mars' axial tilt is perpendicular to the sun, and it is neither polar night nor day. As expected, the periods surrounding the vernal and autumnal equinoxes in the north and south, and to either side of the aphelion periods, exhibit north-south symmetry (Daerden et al., 2019; Fedorova et al., 2021). Figure 6 combines vertical profiles from high northern (65°N–90°N) and far southern (60°S–90°S) latitudes surrounding both the vernal and autumnal equinoxes (panels a, b, d, e, f, h and i of Figure 2). These periods are characterized by a cold lower atmosphere, increasing from ~140 K near 20 km to ~165 K above 45 km. Temperatures below 35 km are consistently

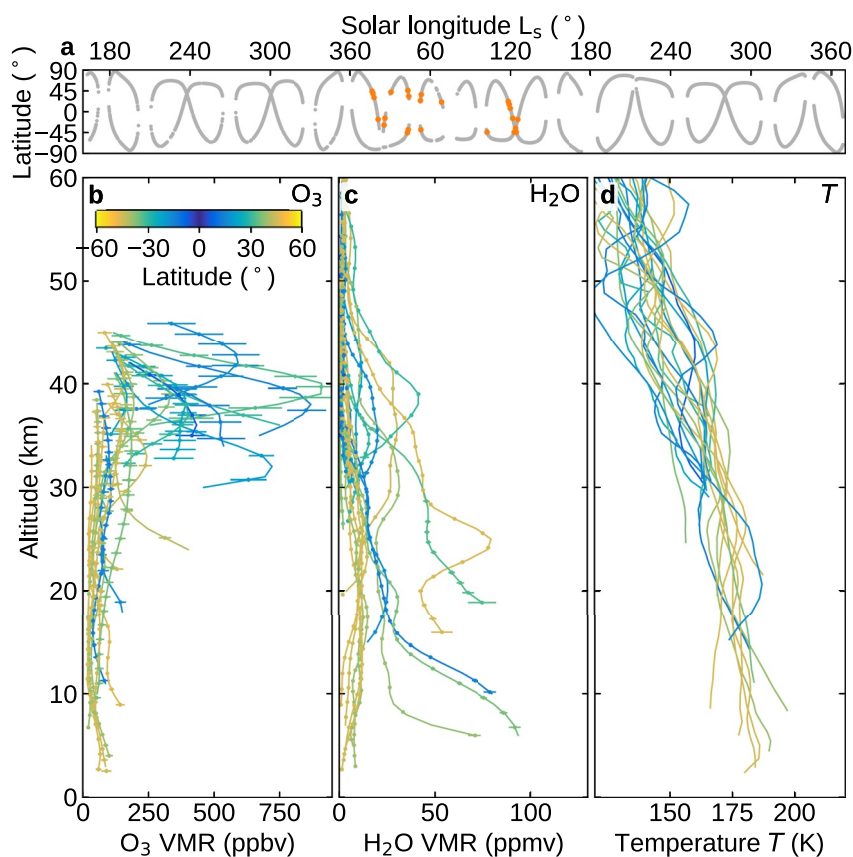


**Figure 6.** Ozone observations during the equinoctial periods. Panel a shows the latitude and  $L_s$  of observations, volume mixing ratio vertical profiles of ozone (panel b) and water vapor (panel c) retrieved from atmospheric chemistry suite mid-infrared (ACS MIR), and temperature retrieved from ACS near-infrared channel (panel d). Colors indicate grouping by time period and hemisphere. These profiles were measured toward the north and south poles around  $L_s$   $0^\circ$  and  $180^\circ$  and correspond to panels b, d, e, f, h and i of Figure 2.

lower during the equinoxes than those shown in Figure 4d from the southern winter (excepting the late southern profiles, yellow in Figure 4d, which are in a transition from the aphelion period to the equinoctial period).

Below 30 km, water vapor abundances rapidly fall, revealing a dry lower atmosphere at these near-polar latitudes. This dry, cold, polar lower atmosphere provides conditions for  $O_3$  to remain in the atmosphere, and we consistently record around 200–500 ppbv  $O_3$  from 25 km to the surface.

A comparison between water vapor and ozone around these periods was made using column abundances measured with SPICAM. Around the equinoxes, Lefèvre et al. (2021) noted a significant difference between the retrieved ozone columns in the northern spring ( $L_s = 0$ – $30^\circ$ ) and northern autumn periods ( $L_s = 150$ – $180^\circ$ ) using data from SPICAM. This was also visible in the LMD GCM simulations. ACS MIR vertical profiles are able to show why there was a difference in the column abundances between the spring and autumn observations. In Figure 6, we show that the equinoctial periods near  $L_s = 0^\circ$  and  $L_s = 180^\circ$  have very similar VMR magnitudes and vertical profile shapes. However, the period  $L_s = 150$ – $180^\circ$  identified by Lefèvre et al. (2021) is too early in this season to exhibit such symmetric behavior. ACS MIR profiles from it are included in Figures 2a, 2c and 5a. In contrast to the profiles shown in Figures 2d and 6a, which feature  $\sim 400$  ppbv  $O_3$  between 10 and 25 km, the profiles from before  $L_s = 180^\circ$  exhibit a sharp decline in  $O_3$  abundance below 25 km. This is due to the late-season persistence of the low-altitude  $H_2O$  layer in northern summer visible in Figure 5. In the SPICAM data, the period following  $L_s = 180^\circ$  also has low column abundances, but matches those obtained at low southern latitudes, which are in agreement with ACS MIR results that show north-south symmetry at this time. During  $L_s = 0$ – $30^\circ$ , SPICAM coverage extends north over the polar vortex region, at the end of a period in which the polar  $O_3$  layer is fully formed and confined below 5 km. Conversely, during  $L_s = 180$ – $210^\circ$ , the SPICAM coverage is pushed



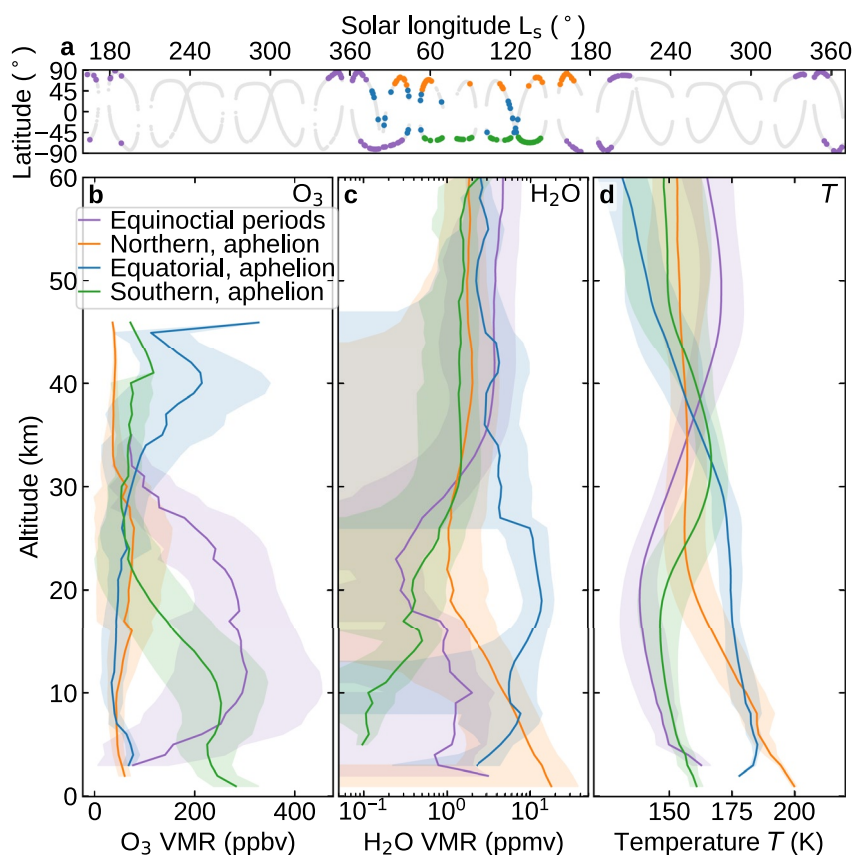
**Figure 7.** Ozone observations made at equatorial and low middle latitudes during the aphelion period. Panel a shows the latitude and  $L_s$  of observations, volume mixing ratio vertical profiles of ozone (panel b) and water vapor (panel c) retrieved from atmospheric chemistry suite mid-infrared (ACS MIR), and temperature retrieved from ACS near-infrared channel (panel d). Colors indicate latitude. These profiles were measured at low latitudes (40°S–40°N) during the aphelion period (southern winter/northern summer) and correspond to panels c and g of Figure 2.

southward, to the periphery of the polar region and at a time when the polar ozone layer has not yet fully formed. Due to the similarity in ACS MIR profiles from these periods (Figures 2a–2e), it is likely that the difference in latitude coverage and the behavior of O<sub>3</sub> below 5 km is responsible for the discrepancy in column abundances.

A unique grouping of observations in the ACS MIR solar occultation data set is during the aphelion period, but at latitudes toward the equator in both hemispheres, between 40°S and 40°N. Compared to the other case studies presented here, observations in this period feature a temperature profile exhibiting a uniform gradient from a warm surface (~180 K) to a very cold upper atmosphere (<130 K at 60 km), shown in Figure 7c. This temperature gradient allows for water vapor of varying abundances to be present below 30 km, but only in trace amounts above (Figure 7b). At these times and latitudes, when ozone is observable, we note very low abundances below 30 km, which are generally the only altitudes where we otherwise detect ozone in our data. Unique to this  $L_s$  range and latitude band, we observe enhancements of ozone of several 100 ppbv at 40 km (Figure 7a). This equatorial ozone layer associated with the aphelion cloud belt becomes more pronounced as observations move from low middle latitudes (25°–40°N/S) toward the equatorial region (25°S–25°N).

The change in water vapor abundance observed in Figure 7 is due to condensation and is caused by the temperature gradient along the vertical. This results in the formation of the well known aphelion cloud belt (Clancy & Nair, 1996; Pearl et al., 2001; Smith, 2004). That seasonal cloud formation would impact O<sub>3</sub> abundance was recognized in early photochemical models (e.g., Clancy & Nair, 1996), and this was observed by SPICAM (Lebonnois et al., 2006). The presence of water ice clouds over this period can be inferred from ACS MIR observations. Aerosol attenuation is visible in an ACS MIR solar occultation sequence of spectra, seen as a reduction in transmission level toward lower altitudes (Olsen, Trokhimovskiy, Montabone, et al., 2021). During the aphelion





**Figure 8.** Mean vertical profiles of ozone and water vapor volume mixing ratios and temperature from the equinoctial periods (Figure 6), and over the aphelion period in the northern hemisphere (Figure 5), the equatorial region (Figure 7), and the southern hemisphere (Figure 4). The shaded regions indicate one standard deviation of the averaged profiles.

period and the equinoctial periods (Figures 2, 5 and 6) attenuation occurs below 10 or 20 km. Over the equatorial region during the aphelion period (Figure 7), however, we consistently see attenuation due to ice aerosols beginning around 40 km, corresponding to the fall in  $H_2O$  VMR at colder temperatures. Separating signals from ice or dust, and quantifying them, is more challenging, but can be accomplished at certain wavelengths when analyzing the continuum of the transmittance, whose shape is solely determined by the particulate components and their broad spectral features (Luginin et al., 2020; Stcherbinine et al., 2020).

Figure 8 summarizes these results by taking the collected profiles in Figures 4–7 and showing their means and standard deviations. During the perihelion period, in which it is summer in the southern hemisphere and dust activity is highest, we are unable to observe ozone at any southern latitudes, and make only occasional observations in the northern hemisphere of low quantities ( $<200$  ppbv) of  $O_3$  below 20 km (around  $50^\circ N$ ). In the aphelion period, during northern summer, we are able to observe  $O_3$  below 30 km, but its abundance strongly is reduced rapidly as observations move toward the surface due to increasing temperatures and water vapor over the same altitude range. In southern winter, we make frequent and consistent observations of  $>100$  ppbv  $O_3$  from between 20 and 30 km to the surface. Between seasons, around both equinoxes in both hemispheres, we observe north-south symmetry in the atmosphere and the highest ozone abundances from 30 km toward the surface.

The comparison is made between  $O_3$  VMR,  $H_2O$  VMR and temperature. Temperature controls the condensation of water vapor. Water vapor photolysis leads to  $HO_2$  formation which converts odd-oxygen to stable  $O_2$ , effectively reducing  $O_3$  concentrations. The production of  $O_3$  from  $CO_2$  photolysis at these altitudes should not change over time due to the stability of  $CO_2$  concentrations and it being well-mixed. Therefore, the observed changes in  $O_3$  VMRs with latitude and season are the result of changes in its loss rate, directly related to temperature and the VMR of water vapor.

Notably, the highest abundances of  $O_3$  observable by ACS MIR above 30 km (low latitudes aphelion, Figure 7) correspond to the coldest observed temperatures at those altitudes. The warmest period is the southern and northern hemispheres around perihelion, and corresponds to when  $O_3$  abundances are low to the point where it is difficult to detect. The periods with the highest  $O_3$  VMRs correspond to those in which the lower atmosphere is coldest (equinoctial and southern aphelion, Figures 6 and 4). While the anti-correlation between  $H_2O$  and  $O_3$  was anticipated, this is the first direct comparison between the vertical profiles of temperature and the abundances of those two species, revealing the direct impact climate has on odd-hydrogen and odd-oxygen in the Martian atmosphere over different altitudes.

## 5. $O_3$ Modeled by the LMD GCM

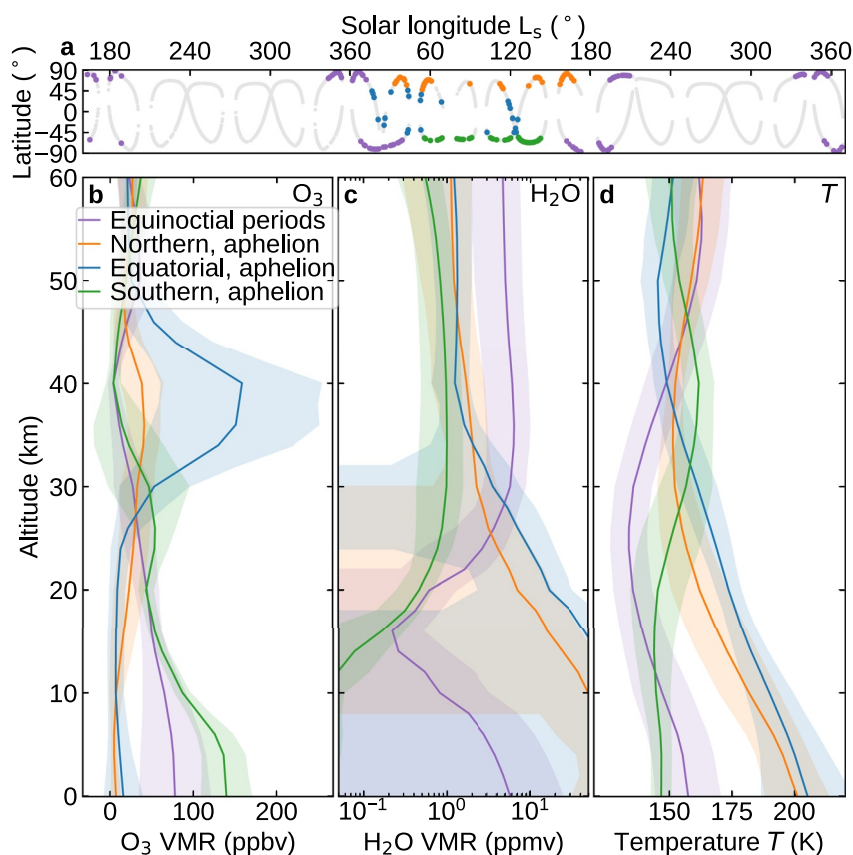
The behavior of ozone in the Martian atmosphere has been extensively studied by contemporary GCMs. Previous efforts using the LMD GCM have shown it can reproduce SPICAM observations in the polar night through modeled transport and photochemistry (Montmessin & Lefèvre, 2013); the Global Environmental Multi-scale (GEM) Mars GCM has been compared to MARCI data (Daerden et al., 2019); and the Open University Mars GCM has been compared to NOMAD data (Patel et al., 2021). However, comparisons with both models to vertical profiles measured with TGO instruments have revealed a discrepancy between the magnitude of modeled and retrieved  $O_3$  VMRs, despite good agreement in  $O_3$  distribution and variability (Khayat et al., 2021; Olsen et al., 2020; Patel et al., 2021). Such discrepancies have been attributed to discrepancies in water vapor abundance which reduces odd-oxygen.

We use here the latest version of the LMD Mars GCM (Forget et al., 1999) with comprehensive chemistry as described by Lefèvre et al. (2021). The atmosphere has been modeled specifically for TGO solar occultations at local terminator times, taking into account the insolation at the ACS MIR solar occultation points over the boundary of the terminator. In the simulations presented here the GCM was integrated with the nominal gas-phase chemistry, with no heterogeneous uptake of odd-hydrogen by water-ice clouds. Included are dust transport and radiative feedback (Madeleine et al., 2012), water vapor and cloud physics (Navarro et al., 2014). The accuracy of the GCM for a specific Mars year depends on constraints from prescribed climatologies (while dust is transported, its column abundance is forced to follow observations) and this run uses dust climatologies for MY 34 and 35 computed as described by Montabone et al. (2015, 2020). The spatial resolution of the LMD GCM is  $3.75^\circ$  in latitude and  $5.625^\circ$  in longitude (note that the movement of the tangent point due to the orbital movement of TGO is on average  $1^\circ$  in latitude over the lower 45 km altitude). Data are produced in both daily and  $5^\circ L_s$  averaged results, and the latter are used herein.

Figure 9 shows the mean profiles extracted from the GCM at the ACS MIR solar occultation points where  $O_3$  was detected, for comparison with the ACS profiles presented in Figure 8. The different trends seen in each seasonal and latitudinal grouping are clearly visible. In Figure 9a, we see that the average ozone VMRs in the GCM are about half those observed, with the magnitudes around the equinoxes and at southern latitudes being around 100 ppbv. ACS MIR observations are  $>200$  ppbv and extend to higher altitudes. The  $O_3$  abundances modeled by the GCM over southern winter are greater than those from the equinoxes, in contrast to ACS MIR observations. Another notable difference is that around northern summer (aphelion)  $O_3$  extends to much higher altitudes in the GCM than the observations. The equatorial ozone layer is very prominent in the GCM data, and the magnitudes of the GCM and the observations are in good agreement, with mean VMRs reaching 200 ppbv.

The magnitudes of low-altitude water vapor also exhibit differences between the GCM and observations. The northern and equatorial regions around aphelion reach  $\sim 100$  ppmv in the GCM, while ACS MIR observations only revealed  $\sim 50$  ppmv. The profile shapes are reproduced, as are the VMRs above 10 km. The temperature profiles exhibit the same shapes and magnitudes (Figures 8c and 9c), with the low-altitude temperatures much warmer in the equatorial and northern regions over the aphelion period (northern summer) than in the south or around the equinoxes. The altitude at which the rate of change is largest (warming or cooling above 30 km), and the subsequent “pause,” is higher in the GCM in each case.

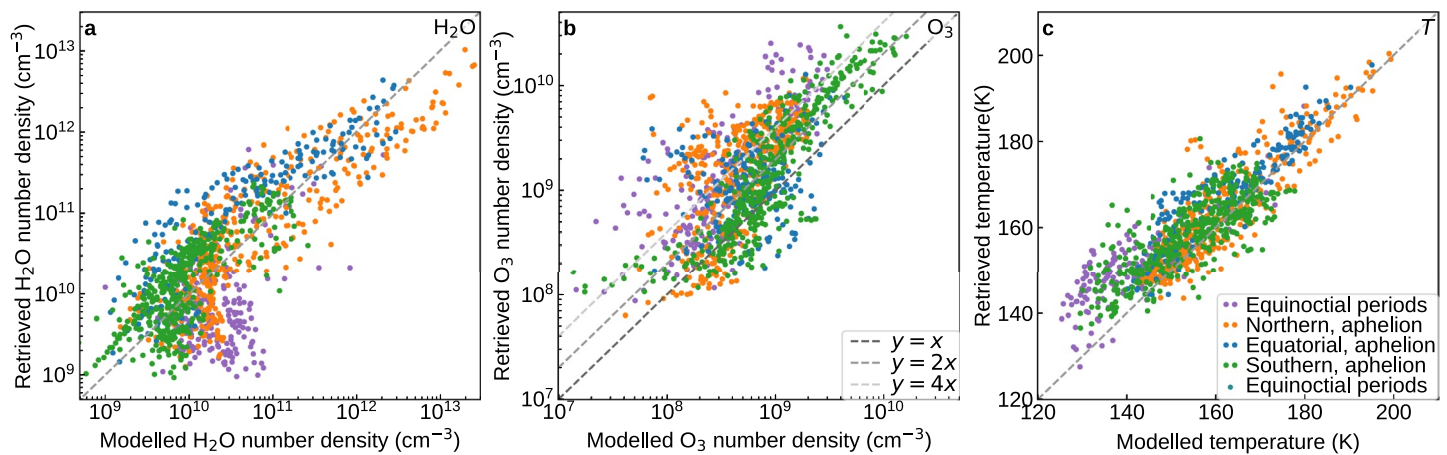
Figure 10 shows a direct quantitative comparison between vertical profiles retrieved using ACS MIR and extracted from the GCM. For each occultation, the vertical profiles from the GCM were interpolated to the pressure levels of the ACS MIR tangent heights where ozone was found. Pressure levels are used rather than tangent heights to mitigate any errors between the estimated heights of ACS MIR and ACS NIR since tangent height is used to



**Figure 9.** Mean vertical profiles extracted from the LMD global climate model (GCM). Shown are ozone volume mixing ratio (VMR) in panel b, water vapor VMR in panel c, and temperature in panel d, as in Figure 8. Each profile was modeled at the local solar terminator time and location of an ACS NIR solar occultation. Profiles are grouped into the equinoctial periods (Figure 6), and over the aphelion period in the: northern hemisphere (Figure 5), the equatorial region (Figure 7), and the southern hemisphere (Figure 4). The shaded regions indicate one standard deviation of the averaged profiles. Lefèvre et al. (2021) noted that for a given column of  $H_2O$ , the LMD GCM underestimated SPICAM  $O_3$  column abundances by about 2 times when using the standard gas-phase chemistry. However, after the inclusion of heterogeneous uptake of OH,  $HO_2$  and  $H_2O_2$  on water ice aerosols was included, differences between the GCM and SPICAM were largely overcome, but these processes remain uncertain.

define the pressure levels. The comparison is done using number densities rather than VMRs since differences in retrieved VMR may result from differences in temperature and pressure (total number density), rather than measured absorption line depths. Number densities facilitate comparison with Lefèvre et al. (2021), and since they are monotonic functions of altitude the axes of Figure 10 reveal higher and lower heights. The three panels in Figure 10 show a comparison between the GCM results and water vapor retrieved with ACS MIR data, ozone VMR retrieved with ACS MIR data, and temperature retrieved using ACS NIR data (Fedorova et al., 2020, 2022). The colors are used to group occultations by the latitude and season, as in Figures 4–8.

In Figure 10a we see reasonable agreement between water vapor retrieved from ACS MIR and modeled by the GCM, with data generally not showing a bias above or below the line of unity, except during the equinoctial periods. At those times, we are observing less water vapor than the model predicts. Since the pressure range for the comparison comes from the ozone retrievals, these data are restricted to the lower atmosphere, where temperatures and water vapor VMRs were among the lowest measured in this study (Figure 8). The profiles extracted from the LMD GCM reveal a similarly low  $H_2O$  VMR with a sharp decrease in water vapor occurring at  $\sim 15$  km (note that for these ozone number density scales in Figure 10, lower altitudes correspond to higher number densities). However, the LMD GCM predicts larger VMRs above 30 km ( $>5$  ppmv compared to  $<2$  ppmv with ACS MIR) and a more prominent surface layer of water vapor, causing the VMR to increase again below 10 km. Due to the relationship between number densities and altitude, large differences in number densities for vertical



**Figure 10.** Comparison of  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , and temperature retrieved from ACS data and computed by the LMD global climate model (GCM). Each retrieved tangent height where  $\text{O}_3$  retrievals were made in an occultation sequence are shown. Pressure levels of the profiles extracted from the LMD GCM are interpolated to those of ACS tangent heights. Panels show: (a)  $\text{H}_2\text{O}$  number density retrieved from ACS MIR and modeled by the LMD GCM; (b)  $\text{O}_3$  number density retrieved from ACS MIR and modeled by the LMD GCM; (c) temperature retrieved from ACS near-infrared channel (Fedorova et al., 2020, 2022) and modeled by the LMD GCM. Dashed gray lines indicated one-to-one correlation. Panel b also has lines indicating when the retrieved  $\text{O}_3$  values are twice, or 4-times the modeled values. Colors indicate groupings of latitude and season.

profiles with similar shapes, as shown in Figures 8 and 9, imply a height mismatch between profile features in the model and observations. Such differences in altitudes where water vapor and ozone are abundant are visible in Figures 8 and 9.

Figure 10b shows the number density of ozone retrieved from ACS MIR data and compared to the GCM. ACS MIR generally observes higher ozone concentrations than predicted by the GCM. This tends to occur in each latitude and  $L_s$  grouping (but notably so in the equinoctial periods, related to the difference in water vapor described above). The difference tends to be on the order of 2–6 times greater, depending on altitude and season. The relative differences between the model and observations change over altitude, as can be seen in Figures 8 and 9 (thus we express the difference as a range). The closest agreement occurs in the southern hemisphere around aphelion, when  $\sim 200$  ppbv  $\text{O}_3$  resides below 15 km, and our observations are 1–2 times the GCM. Periods with larger differences are equinoctial periods, where we find a difference of  $\sim 4$  times. Modeled  $\text{O}_3$  over these periods decreases gradually above 10 km, whereas in the ACS MIR observations  $\text{O}_3$  remains  $\sim 200$  ppbv up to 25 km. Around aphelion in the northern hemisphere we observe  $\sim 6$  times difference. ACS MIR observations reveal  $\sim 50$ – $75$  ppbv below 30 km, with a peak at 25 km. In the GCM, the ozone abundance peaks at 25 ppbv, but at a higher altitude, 35 km. At lower altitudes, the difference grows, and there is only  $\sim 10$  ppbv in the model compared to  $>50$  ppbv in the observations. This is the period in which we may be irregularly and indirectly observing the polar vortex, which will not be reflected in the model. Previous studies have found similar disagreement between models and observations, with a factor of 2 times identified in Olsen et al. (2020) and Lefèvre et al. (2021), and up to 10 times in Patel et al. (2021). These results depend on the amount of water vapor present in the model, which was well constrained when examining SPICAM data (Lefèvre et al., 2021). A more important characteristic to compare with the model than ozone abundance, is the anti-correlation with water vapor, which it is now possible to study at discrete altitude levels for the first time with ACS MIR (Section 6).

The third panel of Figure 10 shows a comparison between LMD GCM temperature profiles and those retrieved using ACS NIR. These are discussed in Fedorova et al. (2020, 2022). From Figures 8 and 9, we see that ACS observations reveal warmer temperatures in the lower atmosphere. A major difference in these subsets of observations is the height of the observed pauses in Figures 8 and 9. This results in a warmer atmosphere above 20 km in the ACS NIR observations, despite comparable, or cooler, temperatures below. Temperature differences between the model and observations have a direct impact on water vapor, but the variation in whether the GCM is warmer or cooler over the considered altitudes range leads to overall agreement in both temperature and water vapor.



Following our discussion of the shapes of the vertical profiles of these three quantities at different seasons and latitude ranges, shown in Figures 8 and 9, we can see that differences in ozone abundances follow differences in temperature and water vapor abundances. Note that while the LMD GCM was run using MY 35 and MY 36 climate data in the form of solar UV flux and dust opacities, it does not incorporate measured temperatures and pressures, which will further constrain ozone photochemistry. Work is ongoing on assimilating ACS, NOMAD and Mars Climate Sounder Data into the LMD and GEM-Mars GCMs which will allow the reassessment of odd-hydrogen production and ozone reaction rates.

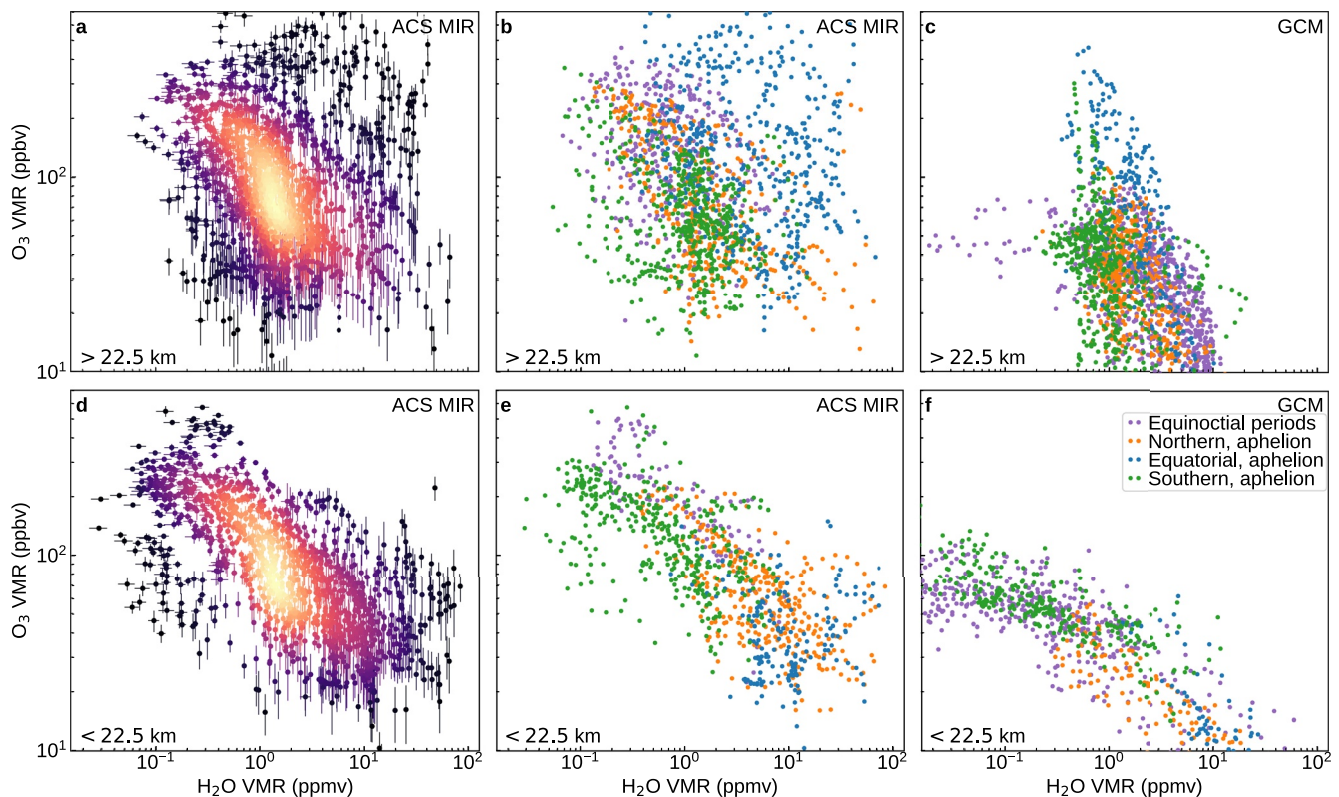
## 6. Relationships Between O<sub>3</sub>, H<sub>2</sub>O, and Temperature

In this section, we will make direct comparisons of the vertical profiles of the VMRs of O<sub>3</sub> and H<sub>2</sub>O measured with ACS MIR. Previously, the column abundances of O<sub>3</sub> and H<sub>2</sub>O measured with SPICAM over four Martian years have been used to quantify the anti-correlation between these species (Lefèvre et al., 2021). SPICAM viewing geometry allows for observations of polar summers, but not winters, and the best agreement in latitudinal coverage between SPICAM and ACS MIR is around the equinoxes when observations of both instruments extend the furthest poleward (noting that O<sub>3</sub> is not detected with ACS MIR over the perihelion period, and that SPICAM observations do not extend south of ~40°S over aphelion). Because of the seasonality of O<sub>3</sub>, SPICAM coverage is greatest at high northern latitudes (>60°N) over the aphelion period. Distinct trends in the SPICAM O<sub>3</sub> and H<sub>2</sub>O comparisons are observed at different time periods, with a stronger reduction in O<sub>3</sub> relative to H<sub>2</sub>O observed during northern summer (L<sub>s</sub> 60°–150°) than in the spring or equinoxes. The O<sub>3</sub> column abundance relative to H<sub>2</sub>O is smaller in the southern hemisphere, although there is symmetry about the autumnal equinox. Coverage is limited in the south because polar winter is not observed and O<sub>3</sub> column abundances in summer are at the detectable limits (<0.5 μm-atm). No correlation was observed at low-latitudes. The nadir SPICAM observations used to derive column abundances are most sensitive to the lowest layers of the atmosphere and the vertical profiles produced by ACS MIR are able to provide more information about the behavior of O<sub>3</sub> and H<sub>2</sub>O at all altitudes.

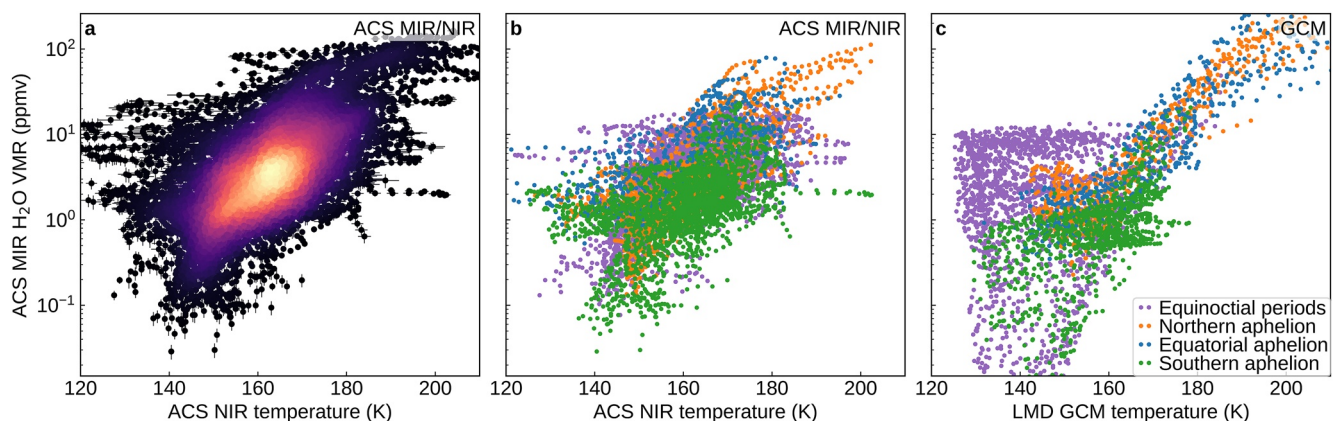
The accuracy, vertical resolution, and sensitivity to temperature, pressure, and multiple trace gases of ACS provide a unique opportunity to probe the relationship between different chemical species. The anti-correlation of ozone and water vapor was noted qualitatively in early observations and repeatedly confirmed (e.g., Clancy, Wolff, et al., 1996; Lefèvre & Krasnopolsky, 2017; Perrier et al., 2006 and references therein) and quantified using SPICAM nadir data (Lefèvre et al., 2021). Figure 11 shows the anti-correlation between retrieved water vapor VMRs and retrieved ozone VMRs for the coincident measurements made with ACS MIR at each altitude where ozone was observed. Panels a and b both contain the same data, with panel a showing the uncertainties of the retrieved data and the density of the observations, and panel b using colors to indicate the latitude and L<sub>s</sub> groupings. Panels d and e similarly contain the same data, but the upper panels only show data measured above 22.5 km, while the lower panels show data below 22.5 km. A large scatter is revealed by these plots, but the density of the data (Gaussian kernel density estimate using the data contained in both panels a and d) shows that the majority falls along a straight line indicating an inverse relationship between the VMRs of both gases, and that even when only small amounts of water vapor are present, rapid depletion of ozone is observed. The altitude division between the upper and lower panels shows that all outliers to the main trend visible in panels a and d come from upper altitudes.

The anti-correlation is not always verified. There is a group of data in the lower middle of Figure 12a that lies just below the main trend, with <50 ppbv O<sub>3</sub> and ~1 ppmv H<sub>2</sub>O. These were collected in the south during aphelion, at the edge of the dry winter polar vortex. There, observations that were made near 20 km exhibit strong gradients in both the O<sub>3</sub> and H<sub>2</sub>O abundances, where ozone is declining and water vapor rapidly increases as altitude grows (Figure 4). Ozone in this period is only observed at low altitudes, around 10 km, and the water vapor is observed to fall rapidly between 20 and 10 km. Another unique subset of observations is that of the equatorial aphelion ozone layer. As water vapor abundance falls and the ozone VMR increases, an apparent minimum water vapor VMR is reached (around 1 ppmv), while the ozone concentration continues to increase above 200 ppbv.

Comparing the data in Figures 11b and 11e, distinguished by whether they are from altitudes above 22.5 km or below, we see that when only the lower altitudes are considered the anti-correlation is much tighter. This excludes the altitude range where both O<sub>3</sub> and H<sub>2</sub>O are changing relative to one another, and indicates that the altitudes



**Figure 11.** Correlation between water vapor and ozone. Panels a, b, d, and e show the simultaneous retrieved O<sub>3</sub> and H<sub>2</sub>O data at each tangent height, where both gases were measured by ACS MIR. The upper panels show data from above 22.5 km, while the lower panels show lower altitude data. Panels a and d include measurement uncertainties and are colored using a Gaussian kernel density estimate, using the full data set (brighter means high density of data points). Panels b and e show the same data as panel a and d, but using colors to indicate the latitude and L<sub>s</sub> groupings used in Figures 4–8. Panels c and f use vertical profiles of H<sub>2</sub>O and O<sub>3</sub> volume mixing ratios extracted from the LMD global climate model for the terminator times at the latitude and L<sub>s</sub> of the ACS MIR occultations used in the other panels (colored as in panels b and e).



**Figure 12.** The correlation between water vapor and temperature. Panels a and b show the retrieved H<sub>2</sub>O from ACS MIR and the coincident measurements of temperature made with ACS near-infrared channel (NIR). The ACS NIR data was interpolated to the pressure levels of the ACS MIR tangent heights. Panel a includes measurement uncertainties and is colored using a Gaussian kernel density estimate (brighter means high density of data points). Panel b shows the same data as panel a, but using colors to indicate the latitude and L<sub>s</sub> groupings used in Figures 4–8. Panel c uses vertical profiles of H<sub>2</sub>O and O<sub>3</sub> volume mixing ratios extracted from the LMD global climate model for the terminator times at the latitude and L<sub>s</sub> of the ACS MIR occultations used in panels a and b (colored as in panel b).

in which VMR gradients are observed have not yet reached a steady state, and there are ongoing processes of photolysis, condensation or sublimation, and chemical reactions.

While the overall anti-correlation is visible in the density plot of the data, the wide variability due to changes in  $O_3$  and  $H_2O$  VMRs over altitude, combined with differences between each of the  $L_s$  groups leads to low Pearson correlation coefficients, which range from  $-0.29$  to  $-0.35$ . Another aspect that affects the anti-correlation that can be explored in the future using a GCM is the impact of local dynamics which would perturb the  $O_3$  and  $H_2O$  abundances.

Figures 11c and 11f show the same thing, but using the vertical profiles of  $H_2O$  and  $O_3$  VMR extracted from the LMD GCM solar occultation run at the latitude and  $L_s$  of the ACS MIR occultations. The anti-correlation between water vapor and ozone reveals a similar inverse trend, but with less ozone being present (and thus a lower slope in panel c), by a factor of  $>2$  when considering the maximum values along the trend being  $\sim 100$  ppbv for the GCM and  $\sim 200$  ppbv for ACS MIR measurements. A difference of this magnitude was also found between SPICAM and the LMD GCM with only gas-phase chemistry (Lefèvre et al., 2021), and is consistent with the differences between model and observation shown in Figure 10. Of note is that there remains a cluster of data below the main trend. These come from the southern aphelion, with VMRs of  $H_2O \sim 1$  ppmv and  $O_3 < 100$  ppbv, and are related to altitudes above 30 km where ongoing changes in the VMRs of  $H_2O$  and  $O_3$  are seen, and water vapor is increasing. Such cases were noted to be the cause of differences between the model and observation during the equinoctial periods as well. The data in Figures 11c and 11f are shown again in Figure S4 in Supporting Information S1 colored by local time, altitude, and latitude.

A second feature that deviates from the trend is the data from the equatorial observations. In the model, the ozone data climb to well over 300 ppbv, but do so in the presence of constant  $\sim 1$  ppmv of water vapor, unlike other time periods where  $>100$  ppbv of ozone was observed. This occurs at the altitudes where the equatorial ozone layer is observed (see Figure S4 in Supporting Information S1 and Figures 8 and 9): the water vapor abundance falls off to  $<5$  ppbv above 30 km, but the  $O_3$  abundance is climbing to 100–400 ppbv. As this is when the aphelion cloud belt is forming, and atmospheric temperatures are continuing to decrease from 30 to 50 km, water ice aerosol formation plays a role in distinguishing the distribution shown in Figure 12c. This agrees with the observations shown in Figures 11b and 11e, in which the upper right region of the plot is also only populated by data from the equatorial observations. There are a few occultations from the southern aphelion grouping in this region of Figures 11c and 11f as well. These were measured around  $L_s = 54^\circ$  north of  $55^\circ S$ , the north-most and earliest observations in this grouping, and close to the equatorial grouping.

In our discussion of Figure 8, we noted that the shape of the ozone profiles appeared to be related to the temperature of the atmosphere, via the condensation of water vapor. Figure 12 shows the correlation between water vapor retrieved using ACS MIR data and the measured temperature profiles from ACS NIR (Fedorova et al., 2020, 2022). A positive correlation is seen between the two measured quantities, with water vapor increasing exponentially with positive changes in temperature. In the equatorial and equinoctial groupings we observe a minimum amount of water that remains in the atmosphere while temperatures decrease toward some of the coldest temperatures presented here. These cold atmospheric conditions occur above 40 km, where the ozone peak is seen, at low latitudes (Figure 7).

Figure 12c again shows the same correlation data, but using profiles extracted from the GCM (and reproduced in Figure S5 in Supporting Information S1 showing local times, latitudes, and altitudes). The GCM reveals similar trends as ACS MIR observations, but only for warmer temperatures. Over the equatorial observations, we see a change in the trend as temperatures fall below 150 K. The data in the upper right corner, from low and mid-latitudes in the northern hemisphere, occur at the lowest observed altitudes, where we are observing the warmer summer near-surface layers of the atmosphere (see Figure S5 in Supporting Information S1). The southern aphelion data is tightly clustered, as it was when comparing ozone to water vapor in Figure 11, but this time the retrieved data is less clustered than the GCM data. A major difference comes from the equinoctial period observations. In the GCM (Figure 9), descending from 50 km, the temperatures fall from  $\sim 180$  to  $\sim 130$  K, while the  $H_2O$  VMRs tend to be fairly constant. From around 30 km toward the surface (Figure 9), temperatures increase again, but the water vapor falls off very rapidly by 20 km due to the cold temperatures. Similar behavior is observed in the retrievals, but to a lesser extent. A difference between the model data and the retrievals impacting this comparison is that the minimum atmospheric temperature occurs at a lower altitude in the ACS NIR data than

in the model computations. The behavior of water vapor at cold temperatures indicates differences in the model regarding condensation and saturation conditions than in our observations.

## 7. Conclusions

We present here three years of data collected by ACS MIR on the ExoMars TGO, covering the second half of MY 34, all of MY 35, and the start of MY 36. ACS MIR operating in solar occultation mode is sensitive enough to measure vertical profiles of the VMR of  $O_3$  using the infrared  $003\leftarrow 000$  absorption band ( $3,000\text{--}3,060\text{ cm}^{-1}$ ). By comparing the vertical structure of simultaneously measured ozone, water vapor, and temperature, we have observed trends in how these important species vary seasonally and exchange hydrogen and oxygen between them. Photochemistry in the Martian atmosphere and the stability of CO and  $CO_2$  depend on odd-oxygen and odd-hydrogen chemistry, and photolysis of  $H_2O$  is the primary source of members of the odd-hydrogen family, while  $O_3$  is an important tracer of odd-oxygen.

We have studied the anti-correlation between water vapor and ozone over altitude for the first time, and observed two altitude layers with peak ozone abundance—a near-surface layer present during the cold and dry aphelion period over a wide range of latitudes, and a layer at 40 km over the equatorial region related to the formation of the aphelion cloud belt. Ozone is generally not observed at most latitudes in either hemisphere during the perihelion period, in which the southern summer creates a warm and water-rich middle atmosphere in both hemispheres. Ozone is commonly observed in both hemispheres around aphelion, when it is fall and winter in the south, and spring and summer in the north, with abundances between 200 and 500 ppbv, which are generally around 2 times larger than GCM predictions for a given amount of  $H_2O$ , but can be greater over specific altitude regions. The northern summer also hosts a near-surface water layer which causes a depletion in ozone below 20 km.

By comparing the vertical structure of ozone, water vapor, and temperature at different latitudes and time periods, we are able to see how the Martian climate controls ozone abundance by varying its rate of destruction, despite the low spatial coverage of solar occultations. Cooling temperatures lead to reduction in the water vapor VMR, and thus a reduction in odd-hydrogen production, which allows  $O_3$  to build up since odd-hydrogen is required to convert odd-oxygen into more stable molecules. The close correlations between temperature and water vapor, and between water vapor and ozone, combined with the observed differences between the expected  $O_3$  abundances and those observed, suggest that the destruction of odd-oxygen by odd-hydrogen is less active on Mars than in current GCM simulations, which do not incorporate heterogeneous chemistry. This may be possibly due to differences in odd-hydrogen production rates, or the reaction rates involving odd-hydrogen species. This will have important implications for the photochemical cycles of water vapor and CO, as well as trace gases, such as HCl and methane.

## Data Availability Statement

The VMR vertical profiles generated in this study are available on the Oxford Research Archive (Olsen, 2022). The data sets generated by the ExoMars Trace Gas Orbiter instruments analyzed in this study are made available in the ESA Planetary Science Archive (PSA) repository, <https://archives.esac.esa.int/psa/#!Table%20View/ACS=instrument>, following a 6 months prior access period, and the ESA Rules on Information, Data and Intellectual Property. Temperature and pressure data used here are from ACS NIR and were generated in other studies. Data from MY 34 are made available in Fedorova et al. (2020) and an updated data version containing MYs 34–36 are published in Fedorova et al. (2022). Data generated with the LMD GCM for TGO solar occultations, along with its user guide, are hosted by LMD and can be found at: [ftp://ftp.lmd.jussieu.fr/pub/forget/TGO\\_SO/](ftp://ftp.lmd.jussieu.fr/pub/forget/TGO_SO/). The subsets of both of these data sources used here are hosted on the Oxford Research Archive (Fedorova, Olsen, & Forget, 2022).

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