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IMPACTS OF HETEROGENEOUS CHEMISTRY ON VERTICAL PROFILES OF MARTIAN OZONE.

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Background

Ozone (O_3) was first detected in the martian atmosphere in 1972 by Mariner 7 and again by Mariner 10 (Barth et al., 1973). Due to its chemical sensitivity and relatively short dayside lifetime (2–3 hours), it is often used as a proxy for other, highly reactive species, which cannot be measured directly with remote sensing (Clancy and Nair, 1996). Such chemical species include hydroxyl radicals (H, OH, and HO_2, collectively known as HO_x), which react with ozone, and participate in its destruction. The two primary destructive pathways of ozone are from UV light (via photolysis) and reactions with HOx species (Clancy and Nair, 1996; Lefèvre et al., 2004). The latter can cause a set of chain reactions which create more HO_x species and lead, in turn, to further ozone destruction. In addition to ozone destruction, HO_x also catalyse the reaction between carbon monoxide (CO) and molecular oxygen (O), recombining to form carbon dioxide (CO_2), the primary constituent of the martian atmosphere. The underlying chemistry of HO_x is thus crucial for understanding the stability of the martian atmosphere, as well as its composition.

HO_x are formed by the photolysis of water vapour, resulting in the well known photochemical anti-correlation between ozone and water vapour. This relationship has been used to understand water vapour transport and seasonal variation (Montmessin and Lefèvre, 2013).

Ozone is underpredicted in martian climate models, implying there are some chemical reactions which are missing or incorrect in models. Heterogeneous reactions of HO_x on the surface of water ice have previously been offered as an explanation for the underprediction of ozone in climate models (Lefèvre et al., 2008, 2021). However, in previous work, including this chemistry has led to an overprediction of ozone (Clancy et al., 2016). In the adsorption of HO_x species, water ice acts as a sink, and the HO_x abundance decreases, allowing the ozone abundance to increase. As a result, the relationship between ozone and water ice has been used as a proxy for the presence of heterogeneous reactions (Clancy et al., 2016). Previous studies with heterogeneous chemistry have only investigated total column abundances of species, which are biased towards low altitude ozone. One way to reduce this bias is to use vertical profile observations with a unit of mass mixing ratio, giving equal weighting across all altitudes.

We investigate reactions between highly reactive HO_x and water ice as a potential explanation for the modelled underprediction of ozone by using a 1-D model and observed vertical profiles from the NOMAD instrument, aboard ExoMars TGO. The vertical relationship between water ice and ozone is used as a proxy for heterogeneous reactions, using profiles from Patel et al. (2021) and Liuzzi et al. (2020). We then use a 1-D model to simulate two water vapour scenarios in order to analyse the ozone – water ice relationship under different circumstances with heterogeneous chemistry. By using a 1-D model, the difference in ozone between the heterogeneous and gas-phase-only chemical simulation can be isolated as purely chemical, without the addition of horizontal transport.

Vertical Cross-Correlation

Vertical profiles are divided into two groups: high northern and high southern latitudes ($> 45°$) from $L_S = 0° - 180°$. The two regions have contrasting water vapour abundances during this time of year, with the southern and northern latitudes having a low and high vapour abundance respectively. We conduct a vertical cross-correlation between observed profiles of ozone and water ice from the NOMAD instrument to identify any relationship within the two regions.

The cross-correlation technique is often used in terrestrial studies between two time series, in order to determine if there is a correlated time lag between the variables. It also determines the strength of the correlation, as well as the length of the time displacement lag (e.g. Arattano and Marchi (2005); Peppa et al. (2017)). A cross-correlation is often used when one variable is expected to influence the other, with some delay in the response. In this study, altitude (rather than time) is displaced in order to identify any vertical patterns between the ozone and water ice, which, due to the adsorption of HO_x in water-ice clouds, may impact ozone across different altitudes. If there is any variation of ozone in the water-ice cloud, this may be detected by the vertical cross-correlation within a few kilometres displacement.
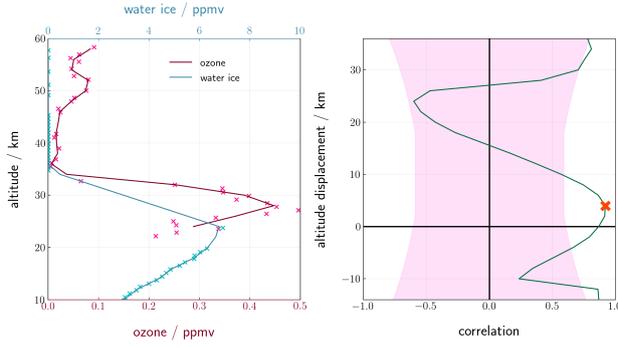
Figure 1: A cross-correlation on a pair of profiles: (left panel) vertical profiles of (blue) water ice and (red) ozone; crosses are datapoints and lines are the interpolated profiles every 2 km; (right panel) the (green) vertical correlation between the profiles across all displacements. A positive displacement of 4 km corresponds to a shifting of the water ice profile up by 4 km. The pink area marks the correlations which are not significant according to a Student's T-test at 5% significance. The red cross indicates the most significant vertical correlation of the cross-correlation. Profiles are from NOMAD/TGO at $L_S = 187°$, latitude 70.5° S, 2020.04.21 11:04:57 UTC.

Figure 1 shows an example cross-correlation between a pair of vertical profiles. The left panel shows the (red) ozone and (blue) water ice vertical profiles, while the right panel shows the correlation of the profiles at different altitude displacements. The highest correlation occurs at -10 km displacement, when the peak in water ice is 10 km below the peak in ozone. This analysis was conducted on all water ice and ozone pairs for both latitudinal regions, which met certain minimum conditions. Such conditions consisted of minimum values and a minimum number of datapoints within each profile.

1-D Model

The 1-D model used in this work is derived from the Open University modelling group Mars GCM (MGCM), which exists as a collaboration between the Laboratoire de Météorologie Dynamique (LMD), the Open University, the University of Oxford, and Instituto de Astrofísica de Andalućia (Forget et al., 1999).

The heterogeneous chemical scheme has been modified from the ASIS scheme from Cariolle et al. (2017), used in Lefèvre et al. (2021), to better represent the adsorption of HO_x as a sink. This is done by adding chemical species which represent the adsorbed status of HO_x, as given by the following;

$$OH + ice \rightarrow ice_{OH}, \qquad (1)$$
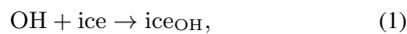
where ice_{OH} is an example of the added species.
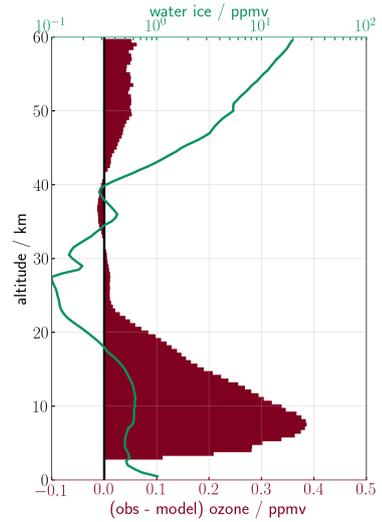

Figure 2: Averaged profiles (212 vertical profiles) > 45° S between $L_S = 100° - 120°$ of (green line) observed water ice, and (red bars) the difference in ozone (observed – modelled). Positive values indicate an underprediction of ozone. Modelled data are taken from the MGCM, assimilated with temperature and dust retrievals from Mars Climate Sounder.

Two scenarios with a high and low water vapour abundance are simulated with the 1-D model to represent high northern and southern latitudes respectively. The scenarios are a simplified representation of high latitude regions and during the aphelion season. To reduce the parameter differences between the high and low water vapour scenarios, the latitudes and local times are kept consistent at latitude 0° and 1200 local solar time (LST); only the time of year is changed, with the low and high water vapour scenario at $L_S = 60°$ and $L_S = 180°$ respectively. The solar insolation is lower in the $L_S = 60°$ simulation, resulting in a lower water vapour abundance due to lower temperatures.

Results

Ozone is currently underpredicted by martian GCMs in both total column abundance and vertical profiles (e.g. Daerden et al. (2019); Lefèvre et al. (2008); Patel et al. (2021)). Comparing vertical profiles observations with simulations, the ozone deficit coincides with increases in water ice abundance, as seen in Figure 2.

From the cross-correlation, we find a positive vertical correlation between ozone and water ice observations at high southern latitudes when water vapour abundance is low. The left panel of Figure 3 shows a histogram of the significant correlations from each set of cross-correlations of ozone and water ice profile pairs. The histogram shows the altitude displacement, binned ev-
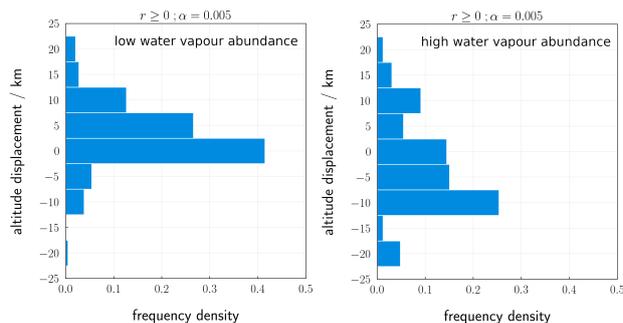
Figure 3: Histogram of altitude displacements for significant, positive, vertical correlations between ozone and water ice observed profiles for (left) southern latitudes ($> 45°$ S) $L_S = 0° - 180°$ and (right) northern latitudes ($> 45°$ N) between $L_S = 30° - 180°$. α shows the significance level, and $r \geq 0$ indicates positive correlations only. Bins cover 5 km, with the y axis label denoting the centre of the bin (e.g. the 0 km bin includes values from 2.5 km to 2.5 km).

ery 5 km. The frequency density peaks when the altitude displacement is between $-2.5 - 2.5$ km, implying that a large proportion of ozone and water ice profiles have a positive correlation when they are within 5 km of each other.

In contrast, there is no such clear peak in the histogram for the high northern latitudes (right panel, Figure 3). The altitude displacements are spread across multiple bins without any distinguishing peaks. This suggests that there is no clear vertical relationship between ozone and water ice. At the high northern latitudes, the water vapour abundance is high, which may impact the effect of heterogeneous chemistry on ozone.

A key difference between the two regions is the water vapour abundance; northern latitudes have a high water vapour abundance, while the southern latitudes have a low vapour abundance.

We replicate these conditions in a 1-D model with simplified scenarios of high and low water vapour abundance. By comparing the difference in ozone with a heterogeneous and gas-phase-only model, we can isolate the effects of heterogeneous chemistry on ozone. There is a large ozone difference between the heterogeneous and gas-phase-only run for the low abundance simulation, occurring when water-ice clouds form. At these altitudes water ice is present, the HO_x abundance decreases significantly, and, as a result, ozone abundance increases, as the ozone destruction rate decreases.

On the other hand, the ozone difference in the high vapour scenario is minimal. The HO_x abundance is much greater and, despite the water ice abundance being three times greater than in the low vapour scenario, the reduction in HO_x has little effect on ozone. This is due to the high HO_x abundance, formed by water vapour photolysis. The heterogeneous reactions remove a smaller relative amount of HO_x, resulting in a high HO_x abundance still available to destroy ozone. The adsorption of HO_x onto water ice under such circumstances is dominated by the high HO_x abundance, and there is little difference in ozone between the heterogeneous and gas-phase-only simulation.

Conclusions

By using a combination of vertical profile observations and 1-D modelling, we find that the water vapour abundance affects the impact that heterogeneous reactions have on ozone.

When water vapour abundance is low, HO_x is adsorbed at altitudes water ice is present, lowering the HO_x abundance, and thus allowing ozone to form. This is shown in the 1-D model where there is a large ozone difference in favour of the heterogeneous simulation in the low vapour scenario. Similarly in the vertical profile observations, there is a strong, positive correlation between ozone and water ice at high southern latitudes when vapour is low. Using this relationship as a proxy, the results from the vertical cross-correlation could indicate heterogeneous chemistry.

In areas of high water vapour abundance, the amount of HO_x adsorbed relative to the total HO_x abundance is minimal, and there is little difference in ozone between the heterogeneous and gas-phase-only simulation. Therefore, it can be expected that the effect of heterogeneous chemistry cannot be observed through the variation in ozone abundance. The positive relationship between ozone and water ice, which is used as a proxy for heterogeneous chemistry, is not expected to be present under circumstances with high water vapour abundance. The lack of a clear vertical correlation between ozone and water ice at high northern latitudes can be explained by the high water vapour abundance (and hence high HO_x abundance).

The inclusion of heterogeneous chemistry could be used to explain at least some of the ozone deficit seen in GCMs, especially when water vapour abundance is low.

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