Modelling the Influence of Oxidative Chemistry on Trace Gases in the Present-Day Atmosphere of Mars

B. S. Gregory, **K. S. Olsen**, *Department of Physics, University of Oxford, Oxford, UK (bethan.gregory@physics.ox.ac.uk)*, **E. Millour,** *Laboratoire de Météorologie Dynamique (CNRS/SU/IPSL), Paris, France*, **M. A. J. Brown**, *Centre for Atmospheric Science, University of Cambridge, Cambridge, UK,* **M. R. Patel, K. Rajendran, P. M. Streeter,** *School of Physical Sciences, The Open University, Milton Keynes, UK*.

Introduction:

The ExoMars Trace Gas Orbiter (TGO) has detected and characterised trace gases in the atmosphere over several Mars years. The data of TGO have provided a much clearer picture of the presence, distribution, and variation of these atmospheric constituents, or their absence and upper limits. The wealth of data obtained has addressed several open questions about the nature of Mars' atmosphere, while other measurements have revealed much that remains poorly understood. For example, models continue to struggle to reproduce ozone distributions, both spatially and temporally, as well as seasonal variations in atmospheric oxygen (O_2), suggesting that some key photochemical interactions may be missing in models. As another example, despite seven years of dedicated observations producing very low upper limits on atmospheric methane levels, there remains no unifying hypothesis that simultaneously explains the detections reported by other Mars assets at Gale Crater [e.g., 1-4].

Chlorine species and oxidative chemistry:

Hydrogen chloride—detected for the first time with TGO [5,6]—has been investigated recently using the mid-infrared channel on TGO's Atmospheric Chemistry Suite (ACS MIR) [7,8]. HCl observations (Figure 1) show a strong seasonal variation, with almost all of the detections occurring during the latter half of the year between the southern hemisphere vernal and autumnal equinoxes (solar longitudes 180-360°), when water vapour is present in the Martian atmosphere and ozone concentrations are low. In addition, there are unusual measurements of HCl, localised in both time and space, near aphelion.

Chlorine-bearing species such as HCl are important to understand in Mars' atmosphere because on Earth they are involved in numerous processes throughout the planetary system, including volcanism. Chlorine species play a key role in atmospheric chemistry: they influence oxidative chemistry and variations in O_2 and O_3 concentrations (e.g., by catalysing the destruction of ozone), and by extension, CH_4 in the Martian atmosphere [9]. However, much remains unknown about original source and sinks of HCl, as well as the factors controlling its distribution and variation, and the way that these factors may have varied in the past.

Here, we use the Mars Planetary Climate Model—a 3-D global climate model that includes a photochemical network—to investigate potential mechanisms accounting for patterns in ozone and HCl detections and interactions between them. These include the correlation of HCl with water vapour and the anti-correlation with ozone. We begin with the role of heterogeneous chemistry involving ice and dust aerosols, by implementing modelling developed for the Open University Mars Global Climate Model [10] and building on existing chlorine photochemical model networks [11,12,13,14]. Heterogeneous chemistry affects the abundances of oxidative species such as OH and HO_2, and by extension, O and O_3. In addition, we investigate how such processes can

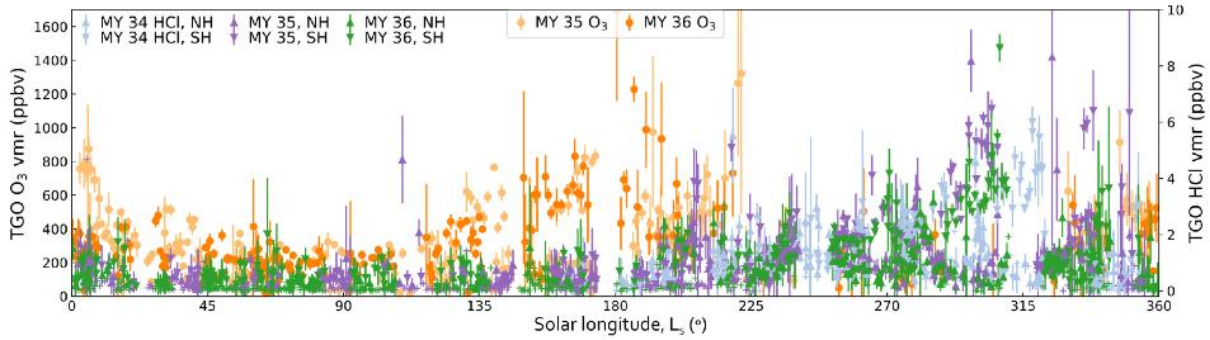

Figure 1: Observations of O_3 and HCl from TGO's ACS instrument, seasonally and across multiple Mars Years [8]. MY=Mars Year; NH/SH=northern/southern hemisphere. Figure from Kevin Olsen.

potentially serve as a mechanism for direct release and sequestration of HCl from the atmosphere. We also explore potential mechanisms behind the annual occurrence of spatially-constrained aphelion HCl, including volcanic sources, and we investigate the interplay between chlorine-bearing species and OH, HO_2, O, and O_3.

Understanding the role of oxidative chemistry on HCl and other trace gases is key to achieving a more complete picture of processes occurring in the present-day Mars atmosphere, as well as processes that have shaped its evolution and habitability.

References:

[1] Giuranna, M., *et al.* (2019). *Nat. Geosci.* 12, 326–332.

[2] Korablev, O. *et al.* (2019). *Nature* 568, 517–520.

[3] Montmessin, F. *et al*. (2021). *Astron. Astrophys.* 650, A140.

[4] Webster, C. R. *et al.* (2015). *Science* 347, 415-417.

[5] Korablev O. I. *et al*. (2021). *Sci. Adv.*, 7, eabe4386.

[6] Olsen K. S. et al. (2021). *Astron. Astrophys*., 647, A161.

[7] Olsen K. S. *et al*. (2024a). *JGR*, 129, e2024JE008350.

[8] Olsen K. S. *et al.* (2024b). *JGR*, 129, e2024JE008351.

[9] Taysum, B. M. et al. (2024). *Astron. Astrophys*., 687, A191.

[10] Brown M. A. J. *et al*. (2022). *JGR*, 127, e2022JE007346.

[11] Rajendran, K. *et al*. (2025). *JGR: Planets* 130(3), p.e2024JE008537.

[12] Streeter, P. M. *et al*. (2025). *GRL* 52(6), p.e2024GL111059.

[13] Benne, B. *et al*. (2024). *EPSC*, pEPSC2024-1037.

[14] Benne, B. *et al*. (accepted). *A&A*.