Martian Atmospheric Chemistry of HCl: Implications for the Lifetime of Atmospheric Methane

Benjamin M. Taysum[1,2,3], Paul I. Palmer[2,3], Mikhail Luginin[4], Nikolay Ignatiev[4], Alexander Trokhimovskiy[4], Alexey Shakun[4], Alexey Grigoriev[5], Franck Montmessin[6], Oleg Korablev[4], and Kevin Olsen[7]

[1] Institute of Planetary Research, German Aerospace Center (DLR), Germany
[2] School of GeoSciences, University of Edinburgh, UK
[3] Centre for Exoplanet Science, University of Edinburgh, UK
[4] Space Research Institute (IKI), Russia
[5] Research School of Astronomy and Astrophysics, Australian National University, Australia
[6] LATMOS/IPSL, Universit´e Paris-Saclay, Sorbonne Universit´e, CNRS, France
[7] School of Physical Sciences, The Open University, UK

Abstract

We develop a 1-D atmospheric photochemistry model for Mars to interpret HCl profile measurements collected by the ACS MIR spectrometer aboard the ExoMars Trace Gas Orbiter (TGO) in Mars Year (MY) 34. We include a gas-phase chlorine chemistry scheme and study 1) surface chemistry, 2) hydrolysis, 3) photolysis, and 4) hydration and photolysis of dust grains as possible sources of gas-phase chlorine chemistry. Heterogeneous uptake of chlorine species onto water ice and minerals in Martian dust are loss processes common to all mechanisms. We drive the 1-D model using TGO profile measurements of aerosols and water vapour. Mechanisms 1, 2, 3 three result in significant model biases. Seasonal variations of Martian HCl are best reproduced by mechanism four, yielding low HCl abundances (< 1 ppb) prior to the dust season that rise to 2-6 ppb in southern latitudes during the dust season. We find that the additional Cl atoms released via mechanism four shortens the atmospheric lifetime of methane by a magnitude of 10^2. This suggests the production of Cl via the UV (or other electromagnetic radiation) induced breakdown of hydrated perchlorate in airborne Martian dust, consistent with observed profiles of HCl, helps reconcile observed variations of methane with photochemical models.

Heterogeneous Release Mechanisms

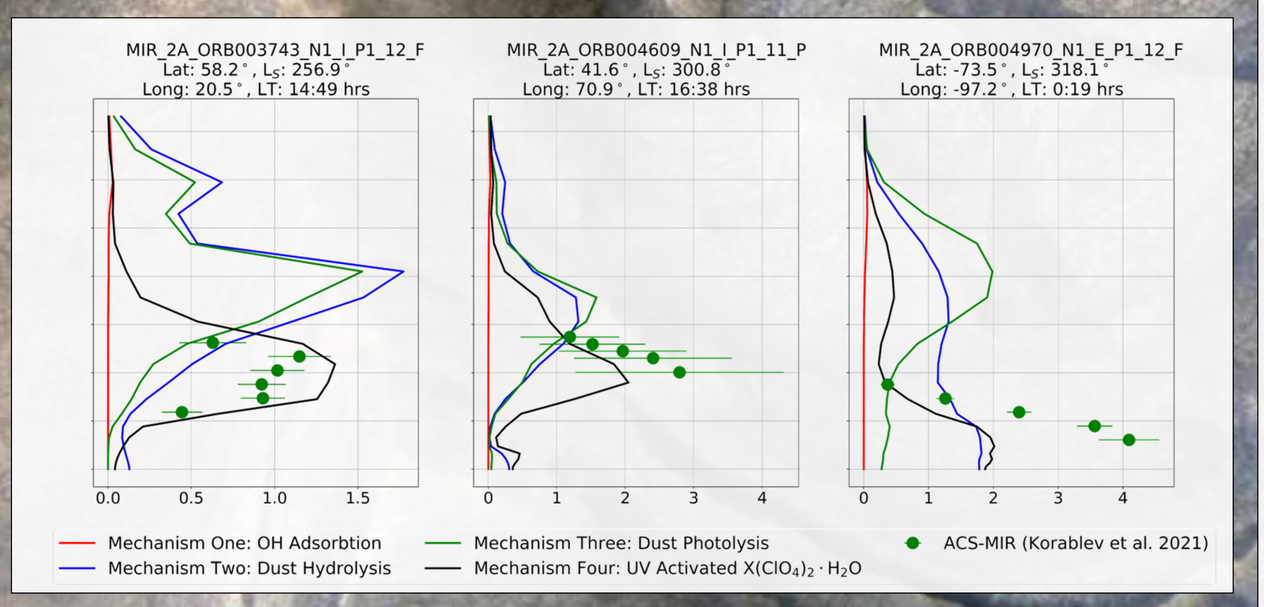
Heterogeneous Reaction	Uptake Coefficient (γ)	Citation
Release Mechanism One: OH Dust Adsorption		
$2OH + Dust_{XCl} \longrightarrow Cl_2 + 2OH$	$0.2/(1 + RH^{0.36})$	George and Abbatt (2010)
Release Mechanism Two: Dust Hydrolysis		
$3H_2O_{(g)} + Dust_{AlCl3(s)} \longrightarrow 3HCl + Dust_{Al(OH)3(s)}$	8E-6	This Study
Release Mechanism Three: Dust Photolysis		
$Dust_{X(ClO_4)_2} + h\nu \longrightarrow Cl + 4O + Dust_{X(ClO_4)}$	1E-4j_clo	This study
Release Mechanism Four: UV Activated Hydrated Perchlorate		
$H_2O_{(g)} + h\nu + Dust_{X\cdot(ClO_4)_2^-} \longrightarrow Cl + 4O + Dust_{X\cdot(ClO_4)^-}$	1E-3 × j_clo × RH	This Study
Heterogeneous Chlorine Uptake Reactions		
$HCl + Dust_{CaCO3} \longrightarrow$ Products	MIN(2.17E-8T^3 - 1.64E-5T^2 + 3.35E-3T - 1.06E-1, 0.1)	Line of best fit of Huynh and McNeill (2021) and Huynh and McNeill (2020)
$HCl + Ice \longrightarrow$ Products	$\frac{0.9\times(1-\theta_{Lang})}{1+(A_D/A_R)\exp(-\Delta E/RT)}$	Hynes et al. (2001)
$Cl_2 + Dust \longrightarrow$ Products	1E-5	Burkholder et al. (2019) upper limits
$ClO + Ice \longrightarrow$ Products	1E-4	Burkholder et al. (2019) upper limits

Reproducing ACS MIR Observations

We find 77 HCl profile observations from ACS MIR (1) in MY 34 that have approximately spatio-temporally collocated (+/- 5° latitude and solar longitude) ACS TIRVIM aerosol profiles (ice and dust mmr and effective radii) and NOMAD observed H_2O vapour profiles (2).

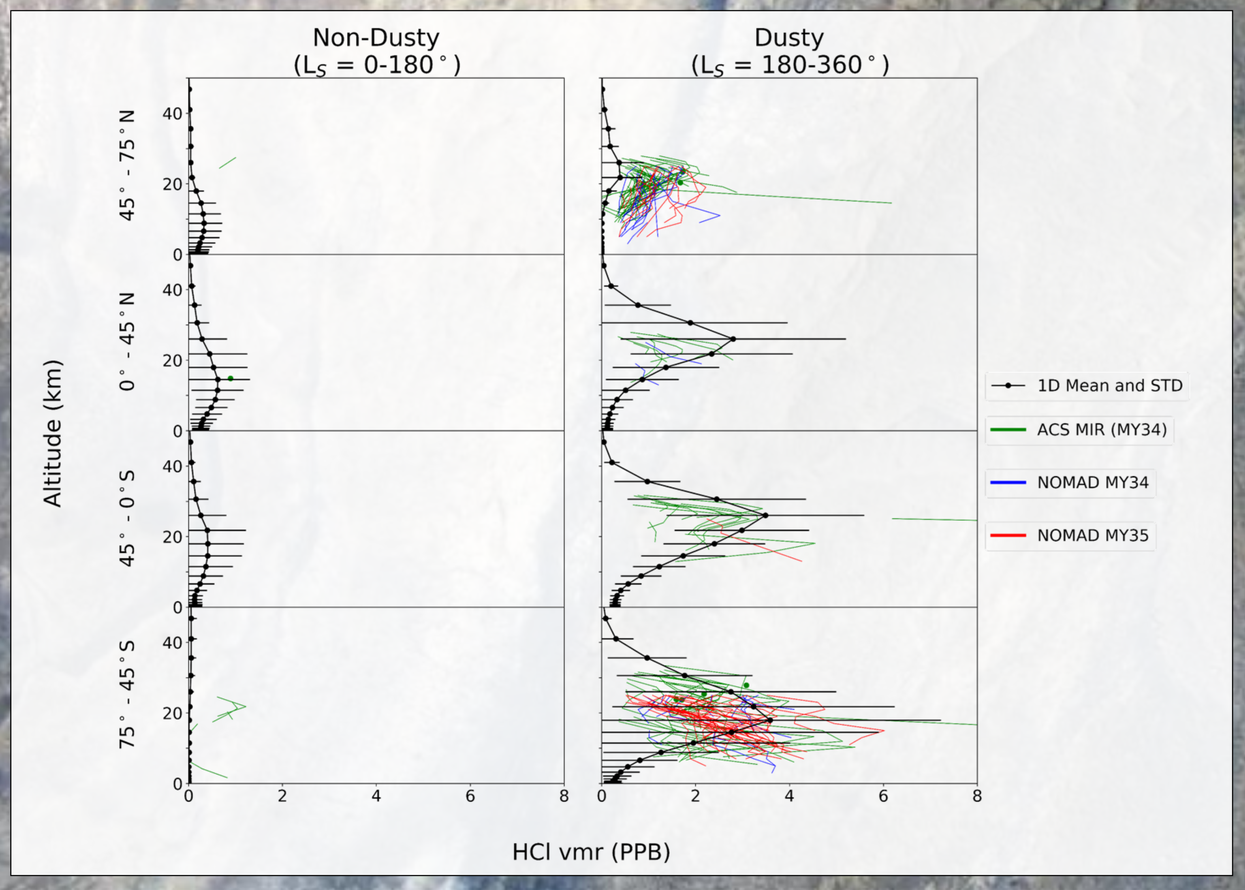
The four hypothesised release mechanisms are tested by driving the 1-D model with MCDv5.3 zonal mean temperature, pressure, and opacity values as well as long-lived trace gas species (CO_2, CO, O_2, H_2) from the MCDv5.3 "dust storm" climatology runs, interpolating with respect to latitude, L_S, local time, and altitude.

The model has a spin-up at the targe observation's latitude and solar longitude of 100 sols (timestep of 0.5 hours) using the MCDv5.3 aerosols and H_2O profiles, after which ACS TIRVIM and NOMAD profiles are inserted. The HCl profiles are extracted one sol after, at the corresponding ACS MIR observations local time.



Seasonal Behaviour of HCl

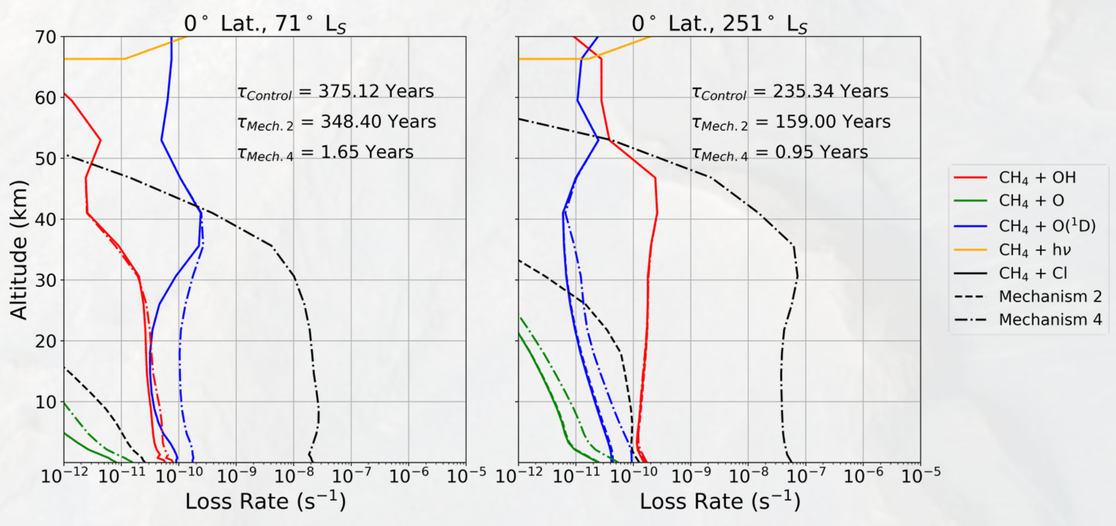
Mechanism 4 is studied by driving the 1-D model with standard climatological atmospheric variables from the MCDv5.3, with a spin-up of 100 sols to enable a diurnal steady state of HCl to be produced. The model is run across latitudes 75° S to 75° N in intervals of 15° and L_S range 0° to 360° in intervals of 30°. The diurnal mean HCl profiles of the runs, discretized in space and time intervals listed in the plot below, are found, and the means are plotted with the errorbars displaying their standard deviations. The observations of ACS MIR (MY 34) and NOMAD (MY 34 + 35) are superimposed in the corresponding subplots.



Implications for Martian Methane

Mechanism 4 introduces Cl atoms directly to the atmosphere from airborne dust. At 298 K, Cl is approximately 16 times more efficient at destroying gas-phase CH_4 than OH. Current photochemical models consider OH to be the dominant CH_4 sink on Mars, yielding atmospheric lifetimes typically > 300 years.

We drive the 1-D model with MCDv5.3 standard climatological parameters at perihelion and aphelion. Comparing the CH_4 lifetime with and without mechanism 4 active, we find that this hypothesised release mechanism can decrease the values by factors > 100 throughout the Martian tropics (latitudes < |45°|).



Conclusions

- Production of HCl via the release of O and Cl atoms from the UV activated decomposition of hydrated dust-bound perchlorates within airborne dust grains is consistent with HCl profiles collected in MY 34 by the ACS MIR.
- Spatio-temporal behaviour of HCl resulting from mechanism 4 is consistent with that observed by ACS MIR and NOMAD throughout MY 34-35.
- Mechanism 4 results in atomic Cl abundances large enough to destroy CH_4 on Mars ≈ 200x faster than standard photochemistry predicts.
  - Elevating the Cl wt % in the dust to 1—1.5%, as observed at the surface by Curiosity, can increase this value to ≈ 600x in localised areas.
  - This mechanism helps to reconcile model and observed variations of methane
- Laboratory studies, in Martian conditions, of the hydrated perchlorate decomposition scheme originally detailed by Zhang et al. 2021 are required to validate and further refine the results of this work.

References

(1) Korablev et al. 2021, *Transient HCl in the atmosphere of Mars*
(2) Aoki et al. 2021, *Annual appearance of hydrogen chloride on Mars and a striking similarity with the water vapor vertical distribution observed by TGO/NOMAD*
(3) Zhang et al. 2022, *Reaction of methane and UV-activated perchlorate: Relevance to heterogeneous loss of methane in the atmosphere of Mars*