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► To cite this version:

Benjamin Taysum, Paul Palmer, Kevin Olsen, Mikhail Luginin, Nikolay Ignatiev, et al.. Observed seasonal changes in Martian hydrogen chloride explained by heterogeneous chemistry. Europlanet Science Congress 2024, Sep 2024, Berlin, Germany. pp.EPSC2024-745, 10.5194/epsc2024-745 . insu-04682909

HAL Id: insu-04682909

<https://insu.hal.science/insu-04682909v1>

Submitted on 31 Aug 2024

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Observed seasonal changes in Martian hydrogen chloride explained by heterogeneous chemistry

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Introduction

The observations of atmospheric hydrogen chloride (HCl) reported in Korablev et al. (2021), Olsen et al. (2021), and Aoki et al. (2021) by the ACS and NOMAD instruments aboard the ExoMars Trace Gas Orbiter (TGO) marked the first detection of a halogen gas on Mars. Its annual appearance, and subsequent disappearance, is observed as being linked to the seasonal cycles of water vapour and airborne dust according to TGO observations taken across three Martian Years (MY34–36; Olsen et al. 2024). The source of HCl is still debated. It is a gas that is commonly associated with marine boundary layer chemistry and volcanic outgassing on Earth – with no surface ocean and little evidence for volcanic outgassing at the Martian surface, HCl's correlations with water vapour and dust and anti-correlations with water ice (Luginin et al. 2024) point to gas-solid (heterogeneous) chemical reactions in the atmosphere as its source, as well as its chemical loss. In this work (Taysum et al. 2024, *Astronomy and Astrophysics*), we present a possible heterogeneous chemistry network that can reproduce the observed vertical profiles of HCl during MY 34, its anti-correlation with water ice, and study its consequences for the photochemical lifetime of methane (CH₄) – the elusive compound that TGO instruments have not yet been able to observe (Korablev et al. 2019, Knutsen et al. 2021) despite the past reports from the Curiosity Rover on the surface (Webster et al. 2015, 2018).

Methodology

We have equipped a 1-D photochemistry model, extracted from the Open University version of the LMD GCM, with 14 gas-phase chlorine species. 68 gas-phase reactions and 9 photolysis reactions are included, and the heterogeneous uptake of HCl onto water ice and calcium carbonate in dust grains is included using reaction rates parameterised in previous laboratory studies. Chlorine (Cl) and oxygen (O) atoms are released by interactions of hydrated perchlorate in airborne dust with UV radiation, as observed in the experimental chamber study of Zhang et al. 2022. Atmospheric profiles of temperature and pressure, and long-lived species such as CO₂, CO, O₂, and H₂, are interpolated from the Mars Climate Database v6.1 across latitude, planet longitude, altitude, local time, and solar

longitude. 77 ACS MIR observations of HCl through MY 34 are studied using approximately colocated ($\pm 5^\circ$ latitude, $\pm 10^\circ$ solar longitude) water ice and dust profiles retrieved by the ACS TIRVIM channel and water vapour profiles retrieved by NOMAD or the ACS NIR channel to drive the 1-D model.

Results

Using our 1-D photochemical model, we find that the release of Cl and O atoms from hydrated perchlorate in airborne dust, and the subsequent fast uptake of HCl onto water ice, is consistent with the spatial and temporal variations of HCl observed by ACS MIR in MY 34 (Olsen et al. 2021) in the 1-D model. Structured atmospheric layers of HCl are also formed where “holes” exist in the vertical profiles of water ice in our model, a phenomena reported by Luginin et al. (2024) when analyzing ACS TIRVIM observations. The resulting HCl profile shapes also share a strong resemblance to the water vapour profiles used in the model, a feature similarly observed by TGO instrumentation (Aoki et al. 2021). As a consequence of the Cl atoms released via our proposed mechanism, the atmospheric lifetime of methane in the Martian atmosphere can be shortened by two orders of magnitude – this could help to reconcile the reported detections of methane at the surface of Gale Crater by Curiosity (Webster 2015; 2018 and Giuranna et al. 2019) with the non-detections in the atmosphere reported by TGO instrumentation (Korablev et al. 2019, Knutsen et al. 2021).