

WHAT CAN DRIVE THE ATMOSPHERIC O₂ VARIATIONS OBSERVED BY MSL SAM? D. Y. Lo¹ (danielloyw@gmail.com), S. K. Atreya¹, M. H. Wong¹, M. G. Trainer², H. B. Franz², T. H. McConnochie³, P. R. Mahaffy², C. A. Malespin², C. R. Webster⁴ and D. Viúdez-Moreiras⁵, ¹Climate and Space Sciences and Engineering, University of Michigan, USA, ²Goddard Space Flight Center, National Aeronautics and Space Administration, USA, ³Space Science Institute, USA, ⁴Jet Propulsion Laboratory, California Institute of Technology, USA, ⁵Centro de Astrobiología, National Institute for Aerospace Technology, Spain.

Introduction: The quadrupole mass spectrometer of the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity rover conducts periodic sampling and measurement of the volume mixing ratios (VMRs) of CO₂, N₂, ⁴⁰Ar, O₂ and CO in the ambient atmosphere [1]. Over the observation period spanning Mars Years (MY) 31–34, the O₂ VMR was found to exhibit significant variation [2]. Even after accounting for transport effects driven by the seasonal condensation and sublimation of CO₂ at the poles that also affect the N₂ and Ar VMRs, the O₂ VMR has residual variations of ~20% (Figure 1). With the photochemical lifetime of O₂ being >10 years [3], variations of such magnitude on a seasonal and interannual timescale are unexpected. Large variations in the O₂ VMR have also been measured in more recent SAM observations, but calibration is still ongoing for these recent measurements. In addition, MSL’s ChemCam spectrometer has observed seasonal and interannual variations in the column-averaged O₂ VMR with relative magnitudes comparable to SAM, although the average ChemCam VMR is higher and only partially correlated with SAM [4].

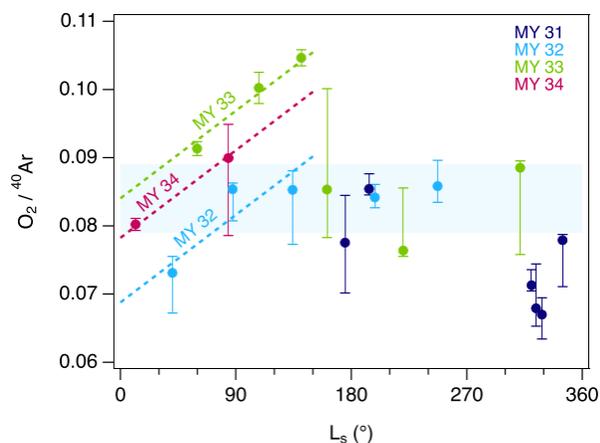


Figure 1: Variations in O₂ VMR, normalized by ⁴⁰Ar VMR, plotted against L_s and colored by MY. The shaded region shows the overlapping mean and median of the dataset. Dashed lines indicate the observed increase in O₂/⁴⁰Ar over L_s 0–150°. Figure from [2].

Correlation with Relative Humidity: After the publication of [2], we discovered a coding error for the

correlation between O₂/Ar and the daily maximum relative humidity as measured by the MSL Rover Environmental Monitoring Station (REMS) [5]. This error affected only the datapoint for sol 45 (Figure 2). The correction increased the Pearson correlation coefficient between the two variables from 0.42 to 0.59.

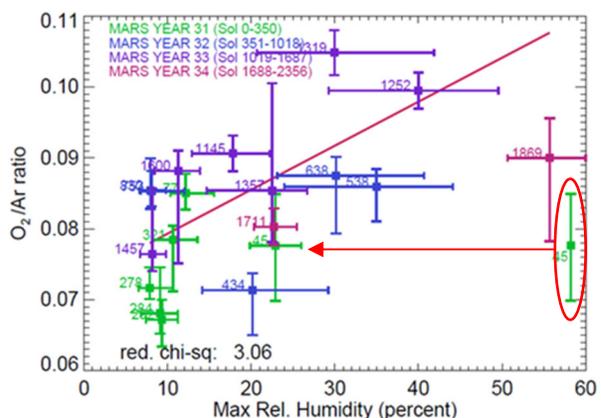


Figure 2: Correlation plot between O₂/Ar and REMS maximum relative humidity. The wrongly plotted point for sol 45 is circled, with an arrow pointing to the corrected point.

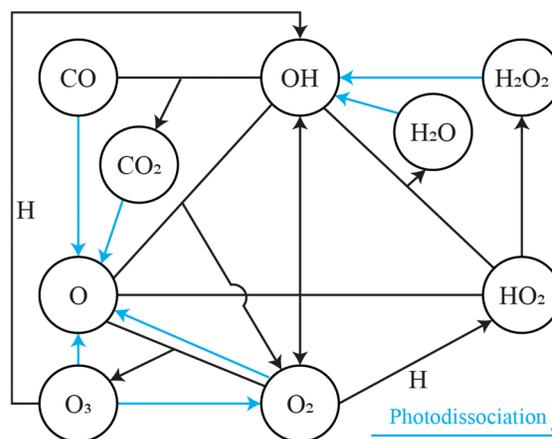


Figure 3: Schematic of oxygen photochemistry. Note that reactions for NO_x chemistry are not shown.

Possible Drivers of O₂ Variations: Drivers for the O₂ variations can lie in atmospheric photochemistry and/or surface processes. The observed variations correspond to 10¹⁴ molecules/cm³ of O₂, and thus the

proposed mechanisms would have to be able to both add and remove this amount of O₂ from the atmosphere over the timescale of ~100 sols.

Photochemistry. O₂ is linked through a web of photochemical reactions to a variety of species, predominantly the photodissociation products of CO₂ and H₂O (Figure 3). In addition to the species and reactions shown in Figure 3, O₂ and O also form a small loop with NO and NO₂, primarily through the reactions NO + O → NO₂ and NO₂ + O → O₂ + NO.

While the observed variations in O₂ VMR are on the order of 10⁻⁴, the combined surface VMR of the minor species is significantly smaller (O – 10⁻⁹, O₃ – 10⁻⁸, OH – 10⁻¹⁴, HO₂ – 10⁻¹², H₂O₂ – 10⁻⁸, NO – 10⁻⁹, NO₂ – 10⁻¹²) [6,7,8]. Thus these minor species are not sufficient to function as reservoirs that can switch between being sources and sinks of O₂ under varying atmospheric conditions, but only as bridges from the larger reservoirs of CO₂, CO and H₂O.

The first step of converting CO₂, CO and H₂O into O₂ is photodissociation (Figure 3). Analysis of the correlation between O₂ VMR and UV radiation fluxes from MSL's Rover Environmental Monitoring Station (REMS) [5] found that while the increase in O₂ VMR is associated with an increase in UV radiation fluxes, there are significant interannual O₂ VMR variations under similar UV radiation fluxes [2]. Thus UV radiation fluxes could at most be a partial explanation for the O₂ variations.

Investigations using the 1-D photochemical model of [8] found that while reasonable O₂ VMRs and a photochemical lifetime of ~100 sols can be achieved (at the surface) through appropriate setting of the surface boundary conditions, the effects of changing these boundary conditions are strongly suppressed above the surface by atmospheric photochemistry. This points to the general stability of the bulk atmosphere against O₂ VMR variations of the observed magnitude, and atmospheric photochemistry is unlikely to be a major driver behind the O₂ variations without the introduction of some yet-to-be-discovered O₂ production channel.

Surface processes. Unlike atmospheric processes which act on a global or regional scale, surface processes can be more spatially limited. The smaller spatial scale implies that we do not need a mechanism for drawing out the O₂ from the atmosphere, and the O₂ decreases can simply be explained by mixing with the background atmosphere. Nonetheless, a surface reservoir and a mechanism for release from the reservoir have to be identified, as well as a mechanism for reservoir recharge.

We identified 3 potential reservoirs of O₂ that can release O₂ under Martian conditions:

1. **Perchlorates:** Perchlorates can decompose to release O₂ when heated or irradiated by galactic cosmic rays [9]. The amount of perchlorates required for producing the observed magnitude of the O₂ variations — a reservoir of at least 15 μg/cm² — can be easily satisfied by the >0.5% perchlorate concentrations at Mars. Nonetheless, the O₂ variations (as opposed to constantly elevated O₂ levels) also require trigger events that activate and deactivate the reservoir, or local mineralogical variations along Curiosity's track.
2. **H₂O₂:** As indicated in Figure 3, H₂O₂ can be photodissociated to form OH, which in turn can react with O to form O₂. Although there is little H₂O₂ in the atmosphere [7], its concentration in the subsurface could be greatly enhanced by diffusion from the atmosphere into the regolith [10], as well as production in the subsurface by processes such as radiolysis [e.g., 9]. The H₂O₂ would then be released by thermal or mechanical triggers [11]. The increase in O₂ would correspond to a reservoir of >6 μg/cm² of H₂O₂. A release of H₂O₂ would also be consistent with the higher relative humidity associated with O₂ increases.
3. **Brines:** O₂ can be dissolved in subsurface brines, and then released when these brines become exposed on the surface and dry up. Based on solubility data from [12], brine reservoirs with depths of 0.1–10⁴ m would be required, with the smaller values corresponding to supercooled Ca(ClO₄)₂ and Mg(ClO₄)₂ brines. While the release of brines containing dissolved O₂ would be consistent with the correlation with higher relative humidity, brine reservoirs of significant depths have not been detected.

Acknowledgments: We would like to thank the MSL team for obtaining the data that this study is based on. This study is funded by the Mars Science Laboratory mission through the NASA Mars Exploration Program.

References: [1] Mahaffy P. R. et al. (2012) *Space Sci. Rev.*, 170, 401–478. [2] Trainer M. G. et al. (2019) *JGR: Planets*, 124, 3000–3024. [3] Krasnopolsky V. A. (2017) *Planetary and Space Sci.*, 144, 71–73. [4] McConnochie T. H. et al. (2021) *AGU Fall Meeting*, Abstract P35A-02. [5] Martínez G. M. et al. (2017) *Space Sci. Rev.*, 212, 295–338. [6] Millour E. et al. (2018) *From Mars Express to ExoMars*. [7] Encrenaz T. (2015) *Astro. & Astrophys.* 578, A127. [8] Lo et al. (2021) *Icarus* 360, 114371. [9] Crandall P. B. et al. (2017) *JGR: Planets*. 122, 1880–1892. [10] Bullock M. et al. (1994) *Icarus* 107, 142–154. [11] Atreya S. K et al. (2020) *JpGU-AGU Joint Meeting*, Abstract MIS07-01. [12] Stamenković V. (2018) *Nature Geosci.* 11(12), 905–909.