EVALUATING ATMOSPHERIC AND SURFACE DRIVERS FOR O_2 VARIATIONS AT GALE CRATER AS OBSERVED BY MSL SAM. D. Y. Lo[1], S. K. Atreya[1], M. H. Wong[1], M. G. Trainer[2], H. B. Franz[2], T. H. McConnochie[3], P. R. Mahaffy[2], C. A. Malespin[2] and D. Viúdez-Moreiras[4], [1]Climate and Space Sciences and Engineering, University of Michigan, USA, [2]Goddard Space Flight Center, National Aeronautics and Space Administration, USA, [3]Space Science Institute, USA, [4]Centro de Astrobiología, National Institute for Aerospace Technology, Spain.

Introduction: The quadrupole mass spectrometer (QMS) 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 CO_2, N_2, ^{40}Ar, O_2 and CO in the ambient atmosphere around the rover [1]. Over the observation period spanning Mars Years (MY) 31–34, the O_2 VMR was found to exhibit significant variation [2]. Even after normalizing for transport effects driven by the seasonal condensation and sublimation of CO_2 at the poles that also affect the N_2 and Ar VMRs, the O_2 VMR has residual variations of ~20% (Figure 1). With the photochemical lifetime of O_2 being >10 years [3], variations of such magnitude on a ~100-sol timescale are unexpected.

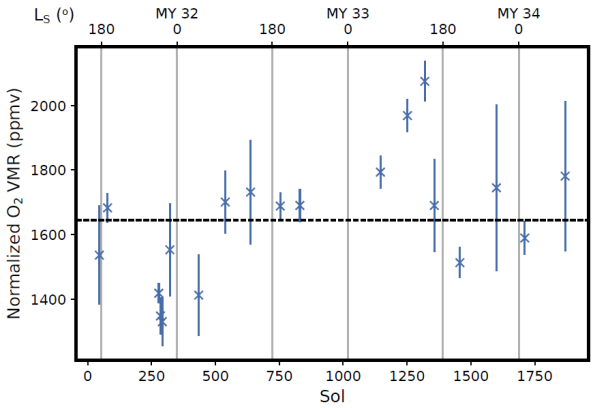

Figure 1: O_2 VMR as measured by SAM QMS up to sol 1909, normalized by the fractional variation of ^{40}Ar VMR measurements about their mean.

We evaluate the possible drivers for these O_2 variations from atmospheric photochemistry and processes in the surface/subsurface. The observed variations correspond to the production or loss of 10^{14} molecules/cm^3 of O_2. We have to find oxygen reservoirs of at least this magnitude to support the variations, and processes that can exchange this required amount of oxygen between the reservoir and the atmosphere over the timescale of ~100 sols.

Atmospheric Photochemistry: O_2 is linked through a web of photochemical reactions to a variety of species, predominantly the photodissociation products of CO_2 and H_2O (Figure 2).

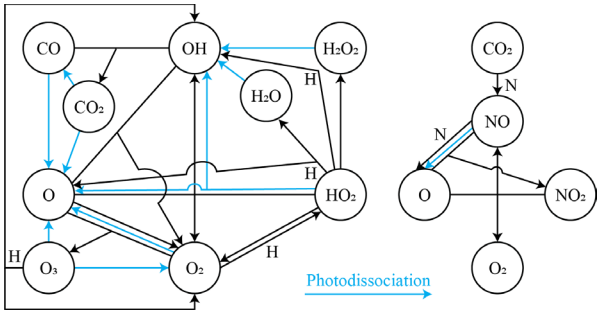

Figure 2: Schematic of oxygen photochemistry.

Only CO_2, CO and H_2O are sufficient large oxygen reservoirs to support the O_2 variations. These species are converted to O_2 through photodissociation, and the O_2 production is balanced by loss directly from O_2 photodissociation, or indirectly through HO_2 photodissociation or reaction with H. We use a 1-D photochemical model [4], with Mars Climate Database [5, 6] atmospheres at different seasons as inputs, to investigate if changes in the O_2 production and loss rates arising from the seasonally varying solar ultraviolet (UV) flux and atmospheric structure and composition can result in the observed O_2 variations. We found the variations in the photodissociation rates to be an order of magnitude too small to be able to fully account for the O_2 variations. Since the photochemical model does not take into account effects from the increased dust and aerosols in the atmosphere around perihelion that would partially cancel out the effects of the increased UV flux [7], the actual contribution to the O_2 variation from photochemistry is likely to be even smaller.

Surface/Subsurface Processes: Any species released from the surface or close subsurface would be subject to atmospheric photochemistry before it was detected by SAM. Thus, before examining specific reservoirs and mechanisms for release, we first investigate what species, when released, can result in an increase of atmospheric O_2 through the setting of a non-zero surface boundary flux for various oxygen-containing species in our photochemical model. We

found that only an O_2 release would be able to drive an O_2 increase.

This narrows our search to O_2 reservoirs at the surface, and we have identified 3 potential reservoirs:

1. *Perchlorates/chlorates*: Perchlorates/chlorates at the surface are maintained by a balance between decomposition from irradiation by UV or galactic cosmic rays [8], and regeneration from the oxidation of Cl_2/chlorides in the presence of O_3/UV [9, 10, 11, 12]. These processes are likely to be facilitated by heterogeneous catalysis. While the amount of perchlorates and chlorates required for producing the observed magnitude of the O_2 variations corresponds to only a 5 cm thickness of regolith assuming typical oxychlorine concentrations [13], decomposition and regeneration rates and their controls are currently too poorly known for accurately modeling their variations over the Martian year. Nonetheless, the role of O_3 in the regeneration of the (per)chlorates is consistent with the observed correlation of increased O_2 with higher H_2O. Higher H_2O would decrease O_3 and perhaps reduce the rate at which O_2 is drawn out of the atmosphere.
2. *H_2O_2*: H_2O_2 can diffuse and be adsorbed into the regolith [14], or be formed from perchlorates through radiolysis [8]. The H_2O_2 would then be released by thermal or mechanical triggers [15], and rapidly converted into O_2 through heterogenous catalysis. However, known rates are too small by 4 orders of magnitude for driving the observed atmospheric O_2 variations.
3. *Brines*: O_2 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 of >1 m thickness would be required, but with <10 wt. % water equivalent hydrogen (WEH) at the Martian surface [16, 17], we would require a >10-m thick brine layer. Given the annual thermal skin depth at Mars is ~1 m, it is unlikely that the O_2 in this brine layer would be fully accessible to fuel the atmospheric O_2 variations.

Correlation with Curiosity's Location: We found no relationship between the atmospheric O_2 variations and the local surface geology and mineralogy along Curiosity's track, as well as the subsurface WEH as measured by MSL's Dynamic Albedo of Neutrons (DAN) instrument [16].

Future Work: While SAM QMS has continued taking atmospheric VMR data through the mission, the data used for this study goes up to only MSL sol 1908. High signal levels from the wet chemistry experiment on sol 1909 apparently caused a shift in the sensitivity of the instrument, and we have been working on a new calibration for the VMR measurements. Curiosity also measures atmospheric O_2 in a column up to ~20 km above the rover using ChemCam through passive sky observations [18]. The higher frequency of these observations would be very useful for investigating the relationship of the O_2 with other variables, in particular H_2O which the passive sky observations also measure [19]. Finally, TGO also measures O_2 globally through solar occultations down to an altitude of ~10 km [20], providing a larger spatial context for interpreting the SAM measurements. We plan to continue the MSL SAM and ChemCam measurements into the future, and integrate the multiple perspectives offered by the different datasets to better characterize these unexpected atmospheric O_2 variations and elucidate their underlying driving processes.

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