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UNEXPLAINED OXYGEN VARIABILITY: NEW RESULTS ON MOLECULAR OXYGEN IN THE LOWER MARTIAN ATMOSPHERE FROM CHEMCAM AND SUPERCAM PASSIVE SKY OBSERVATIONS

T. H. McConnochie, , *Space Science Institute, Boulder CO, USA (tmcconnochie@spacescience.org)*, **M. G. Trainer, M. D. Smith, S. D. Guzewich, H. B. Franz**, *NASA Goddard Space Flight Center, Greenbelt, MD, USA,* **C. E. Newman,** *Aeolis Research, Chandler, AZ, USA.* **D. Y. Lo, S. Atreya,** *University of Michigan, Ann Arbor, MI, USA,* **J. E. Moores, H. M. Sapers,** *Centre for Research in Earth and Space Science, York University, Toronto, Canada,* **M. T. Lemmon**, **M. J. Wolff**, *Space Science Institute, Boulder CO, USA*, **F. Montmessin, E. W. Knutsen,** *LATMOS, Guyancourt, France,* **T. Fouchet, T. Bertrand,** *LESIA, Paris Observatory, France,* **O. Gasnault, J. Lasue, O. Forni**, **P. Pilleri, S. Maurice,** *IRAP, CNRS, Université de Toulouse, UPS-OMP, Toulouse, France,* **C. Legett IV, R. T. Newell, D. Venhaus, N. Lanza**, *Los Alamos National Laboratory, Los Alamos, NM, USA,* **R. C. Wiens**, *Purdue University, West Lafayette IN, USA,* **M. Hecht**, *MIT Haystack Observatory, Westford MA, USA*, **M.-P. Zorzano**, *Centro de Astrobiologia, INTA, Spain,* **A. Khayat**, *NASA Goddard Space Flight Center, Greenbelt, MD, USA and CRESST II, Department of Astronomy, University of Maryland, MD, USA,* **Franck Lefèvre,** *LATMOS, CNRS, Sorbonne Université, UVSQ, Paris, France,* **Frank Daerden,** *Royal Belgian Institute for Space Aeronomy, Brussels, Belgium,* **Anna Fedorova, Alexander Trokhimovskiy,** *Space Research Institute RAS, Moscow, Russia*

Background: MSL's SAM-QMS atmospheric sampling showed that the O_2 volume mixing ratio (VMR) in the near-surface Martian atmosphere has significant seasonal and interannual deviations from the pattern expected and observed for inert non-condensable trace gases (Trainer et al, 2019). Yet photochemical GCM's show that, given known chemistry, O_2 should behave identically to inert trace gases such as argon (Lefevre et al., 2004; Daerden et al., 2019), consistent with photochemical models showing O_2 lifetimes of at least 10 years (Atreya et al., 2006; Lefèvre & Krasnopolsky, 2017).

Trainer et al. (2019) argued that the magnitude of O_2 deviation from inert trace gas behavior is too large to be explained by any atmospheric sources – essentially because CO_2 photolysis is too slow and H_2O vapor abundance is too small – which suggests that some kind of surface reservoir of oxygen is actively exchanging with the atmosphere on seasonal timescales. The Viking Gas Exchange (GEx) experiment's finding of O_2 release from a soil sample upon humidification (Klein, 1978; Oyama & Berdahl, 1977) supports the idea that such a reservoir might exist. Both superoxides and UV-degraded or ionizing-radiation-degraded chlorates & perchlorates have been proposed (Yen et al. 2000, Quinn et al., 2013, respectively) as the source reservoir for the Viking GEx O_2 release, and both superoxides and chlorates/perchlorates have been proposed to form with an atmospheric source for their O_2 (Yen et al. 2000, Carrier and Kounaves, 2015). Thus, there are proposed mechanisms for both directions of a cyclical exchange of O_2 between the atmosphere and surface. We, therefore, can consider a hypothetical surface-atmosphere "oxygen cycle" as a potential explanation for the unexpected O_2 variability; although it remains unclear whether any of these surface-atmosphere exchange mechanisms can operate with the rates necessary to explain the SAM data. Interestingly, both the uptake and release mechanisms for O_2 in surface soils, as they have been proposed, involve exposure to UV or higher-energy radiation, but only the release mechanisms are proposed to involve water vapor humidity. This suggests both a relationship between atmospheric O_2 and the water cycle, an idea that Lo et al. (2022) have already begun to explore, and a potentially complicated relationship with UV-blocking aerosol dust which could limit both uptake *and* release of O_2.

Understanding this apparent surface-atmosphere exchange of oxygen will be important for understanding the formation and likely distribution in space and time of perchlorates and other soil oxidants, which in turn have implications for the preservation of organics on the Martian surface. In addition, having a major active reservoir for O_2 at the surface would potentially complicate the traditional explanation (e. g. Lefèvre & Krasnopolsky, 2017) for the relative abundances of CO and O_2 and their role in recycling CO_2 photolysis products back to CO_2 to stabilize the Martian atmosphere.

Measurements: Both ChemCam on the MSL rover (e.g. Wiens et al., 2012) and SuperCam on the Mars2020 rover (e.g. Maurice et al., 2021; Wiens et al., 2021) perform "passive sky" observations following the technique of McConnochie et al. (2018). No laser is used (hence "passive") and the spectrometer views the sky at two different elevation angles to provide two different path lengths through the absorbing gases. Ratioing the signal from the two different path lengths eliminates instrument response and solar spectrum uncertainties.

The O_2 retrieval technique also follows McConnochie et al. (2018), but in this case fitting the 759 – 767 nm O_2 absorption and updating the molecular line parameters to those from the HITRAN 2016 database. CO_2 absorption lines near 783 nm and 789 nm are used as a reference to correct for the effect of

aerosol scattering uncertainties on line depth. The depth of these O_2 and CO_2 absorption lines is about 0.05% – 0.2% relative to the continuum.

In this spectral region SuperCam uses a transmission spectrometer and an intensifier, while ChemCam uses a reflection grating and no intensifier. Both use nearly-identical CCD detectors. The SuperCam oxygen retrieval precision appears to be limited mainly by fluctuations in intensifier throughput, while for the non-intensified ChemCam it is clear that both systematic and random uncertainties are dominated by detector background. SuperCam and ChemCam thus require very different data processing for passive sky, and with an 8-year head start the ChemCam data processing is relatively mature although some improvements are still planned. SuperCam data processing for filtering intensifier throughput feature is still preliminary and so the results that follow are based solely on the ChemCam passive sky data set.

Both ChemCam and SuperCam passive sky observations are acquired irregularly to minimize conflicts with other rover operations, but we are currently targeting an *average* sampling interval of 14 sols with both instruments. Over the course of the MSL mission, the ChemCam passive sky average sampling interval has been as small as ~7 sols in some periods and as large as ~50 sols in other periods. Since September 2020, we have been adjusting the timing of ChemCam passive sky measurements (without altering the *average* sampling interval) to occur within 1-2 sols of a Trace Gas Orbiter ACS occultation observation (e.g. Korablev et al., 2018) in the vicinity of Gale Crater whenever feasible.

Results:

Long-term Averages. ChemCam O_2 retrievals give 2000 +/- 60 ppm averaged over roughly 180 individual observations spanning about 4.5 Martian years. This is comparable to Trace Gas Orbiter (TGO) ACS occultation results which give ~1900 ppm on average for 15 – 25 km altitudes in the low-to-mid- latitudes (Fedorova et al., EGU General Assembly 2021 presentation materials). MSL's SAM Quadrupole Mass Spectrometer atmospheric samples show notably less O_2 than ChemCam, giving 1610 ± 90 ppm averaged over Mars Years 31-34. Herschel Space Observatory's HIFI observed even less O_2 in Mars Year 30 (@ L_s = 77) reporting a value of only 1400 ± 120 ppm (Hartogh et al., 2010), which was comparable to the previous canonical value of ~1300 ppm from ground based measurements (Barker, 1972; Carleton and Traub, 1972).

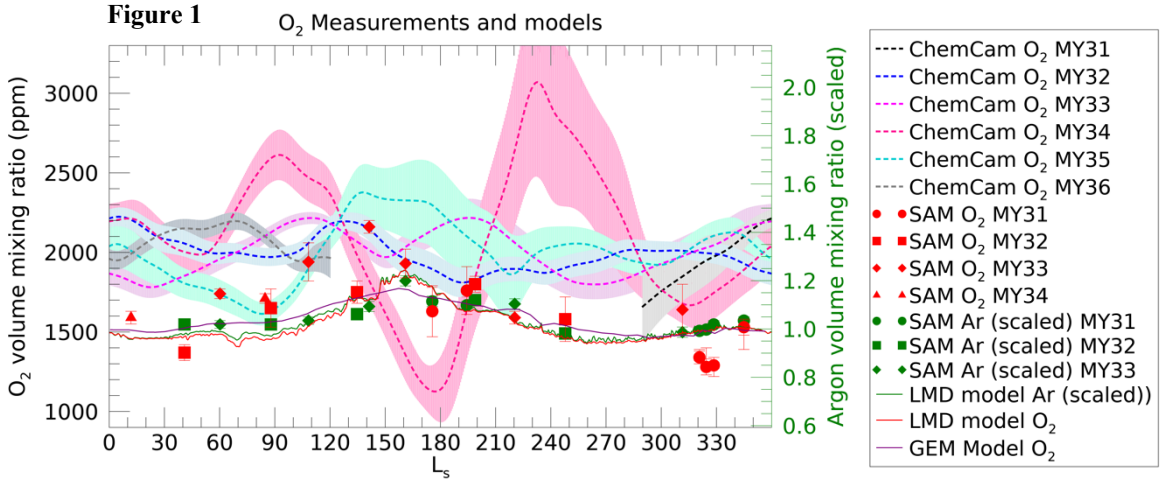
Thus, understanding of Martian O_2 abundances has evolved significantly in recent years from a generally-accepted value near 1300 ppm to a new paradigm of average abundances in the 1600 – 2000 ppm range. Furthermore, the difference between the long term average near-surface SAM O_2 (Trainer et al. 2019), and the long term average column measurement from ChemCam, is statistically robust, and TGO-ACS (Fedorova et al., 2021) tends to corroborate ChemCam. Consequently, there is a strong suggestion that O_2 tends to be depleted near the surface at the equator, which is further evidence of O_2 lifetime being much shorter than the > 10 years in existing models and also fits with a hypothesis that release of O_2 from soil is disfavored at the surface near the equator compared to other locations on Mars due to lower humidity.

Mars Atmosphere O_2 Measurements		
O_2 VMR	**Type and Timing**	**Reference**
2000± 60 ppm	MSL ChemCam, average of MY 31–36	this work
~1900	Trace Gas Orbiter ACS, average of 15-25 km altitudes in low-to-mid-latitudes, MY 3435	Fedorova et al., 2021
1610 ± 90 ppm	MSL SAM, average of MY 31 34	Trainer et al. 2019
1400 ± 120 ppm	Herschel Space Observatory, MY 30, L_s = 77)	Hartogh et al., 2010
1300 ± 130 ppm	Ground based MY 9, L_s ~ 300 - 340	Barker, 1972; Carleton and Traub, 1972

Seasonal cycles and interannual changes. In previous reports on ChemCam O_2 results we had low confidence in the ChemCam evidence of interannual and seasonal variability because the amount of scatter and frequency outliers in the times series was not well explained by our predicted uncertainties. This situation has now changed because the data set has grown sufficiently large and because we have improved the statistics of our smoothed time series by adopting a local regression approach. The local regression finds a smoothed value at a given time by fitting a linear regression to nearby observation points, weighting each observation point by its distance as well as its estimating uncertainty.

In Figure 1 we have suppressed individual observation points in order to show 5 Martian years of the smoothed ChemCam O_2 results with 1-sigma uncertainties represented by the shaded area around each dashed line. Thinner lines with no uncertainty shading are outputs from the LMD (Lefèvre et al., 2004) and GEM (Daerden et al., 2019) photochemical GCM models for comparison. Red points with error bars are SAM O_2 measurements from Trainer et al. (2019), and the green points are Ar from Trainer et al. (2019) to show that the GCM models perform very well for truly inert gases. The season around L_s = 90 stands out as having clearly significant interannual variability in ChemCam O_2 results. Mars Year 34 also shows notably lower ChemCam O_2 than in other years in the L_s = 180 season, just before the Mars Year 34 global dust

Figure 1



storm. The very high value in the post-dust-storm period of Mars Year 34 is based on only one ChemCam passive sky observation with relatively poor precision so its large apparent difference from the values in other years is not actually statistically significant, as is apparent from the uncertainty represented by the shading.

One consequence of the large interannual variability in the L_s = 90 season is that the Herschel O_2 measurement, which happened to occur at L_s = 77, turns out to not be an outlier. Factoring in its uncertainties, it is only slightly smaller than what was observing by ChemCam in MY 35, and, given the wide interannual dispersion, it's entirely plausible that ChemCam might have observed even less in that same season in MY 30 had it been in operation at that time.

Discussion:

The large deviation of ChemCam O_2 from the model expectations, and the lack of a strong correlation and different average values between SAM and ChemCam O_2 are further evidence of oxygen chemistry being more active than in current model expectations because they mean that the O_2 chemical lifetimes cannot be much larger than advections or vertical mixing time scales. ChemCam and SuperCam are sensitive only to the bottom 25 km of the atmosphere, with a 75% weight on the bottom 10 km.

A more novel implication comes from the large interannual variability of O_2 in certain seasons. This suggests that the hypothesized oxygen cycle would be quite sensitive to environmental conditions that are themselves quite variable. The primary season of observed O_2 interannual variability happens to coincide with peak water vapor abundance over northern high latitudes, so, speculatively, variability in that peak humidity and its interaction with surface materials or aerosol opacity could drive variable release of O_2 from the soil, which is then rapidly advected into the column over Gale Crater but perhaps less rapidly transported to the near surface atmosphere in Gale as sampled by SAM.

Adding O_2 measurement over Jezero Crater from SuperCam will serve to further constrain such hypothetical processes. Continuing coordinated observations with TGO-ACS will do so as well. Ultimately, however, the path forward for interpreting O_2 at those multiple sites in terms of processes and preferred locations for surface-atmosphere oxygen exchange will require a GCM that incorporates some representation of the hypothesized surface processes.

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