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COMPARING THE UNEXPLAINED VARIABILITY OF MOLECULAR OXYGEN IN THE MARTIAN ATMOSPHERE TO WATER VAPOR AND ARGON. T. H. McConnochie¹, S. J. VanBommel², D. Y. Lo^{1,3}, E. W. Knutsen⁴, F. Montmessin⁵, T. Bertrand⁶, T. Fouchet⁶, C. Royer⁵, S. Maurice⁷, A. Cousin⁷, R. C. Wiens⁸, M. T Lemmon¹, M. J. Wolff¹, M. D. Smith⁹, A. S. J. Khayat⁹, M. G. Trainer⁹, H. B. Franz⁹, O. Gasnault⁷, J. Lasue⁷, N. Lanza¹⁰, S. K Atreya³, G. Martinez¹¹, F. Lefèvre¹², F. Daerden¹³, M. H. Hecht¹⁴, M.-P. Zorzano¹⁵, D. Viudez Moreiras¹⁵. ¹Space Science Institute, Boulder CO, USA (tmcconnochie@spacescience.org), ²Department of Earth and Planetary Sciences, Washington University in St. Louis, USA, ³University of Michigan, MI, USA, ⁴University of Oslo, Institute for Technology Systems, CENSSS, Norway, ⁵LATMOS, Guyancourt, France, ⁶LESIA, Paris Observatory, France, ⁷IRAP, CNRS, Université de Toulouse, UPS-OMP, Toulouse, France, ⁸Purdue University, West Lafayette IN, USA, ⁹NASA Goddard Space Flight Center, Greenbelt, MD, USA, ¹⁰Los Alamos National Laboratory, Los Alamos, NM, USA, ¹¹LPI/USRA, Houston, TX, USA, ¹²LATMOS, CNRS, Sorbonne Université, UVSQ, Paris, France, ¹³Royal Belgian Institute for Space Aeronomy, Brussels, Belgium, ¹⁴MIT Haystack Observatory, Westford MA, USA, ¹⁵Centro de Astrobiologia, INTA, Spain,

Introduction: O₂ variability in excess of that expected for inert non-condensable trace gases [1] remains unexplained [2]. Photochemical models e.g. [3,4] show O_2 lifetimes of at least 10 years given known chemistry, and consequently photochemical GCMs e.g. [5,6] show a constant ratio of $O₂$ to other noncondensables such as Argon. In contrast, Mars Science Laboratory's (MSL) Sample Analysis at Mars (SAM) instrument suite shows \sim 20% O₂ variability relative to Argon [1], and [1,2] argued that a non-atmospheric reservoir of O atoms was required to supply this level of variability.

As we have previously reported e.g. [7,8] both the ChemCam and SuperCam instruments suites, on MSL and Mars 2020 respectively, measure $O₂$ as well as water vapor and aerosols in the atmospheric column above their respective rovers by performing passivemode spectroscopy of the sky. The essential features of the passive sky gas measurement technique are that it takes advantage of the different atmospheric path lengths from pairs of elevation angles to remove instrumental uncertainties that would otherwise overwhelm weak absorption lines, and that it uses $CO₂$ absorption lines as a reference to correct for the effects of aerosol scattering uncertainties on absorption band depths.

The ChemCam passive sky measurements now span nearly six Mars years with a mean sampling interval of 16 sols. We have steadily refined our measurement techniques and data processing/model fitting over time, and this improved accuracy combined with a now large data set allows us to be confident that much of the surprising O_2 variability observed by ChemCam is robust even though there remain some outlier data points that must still be considered unreliable. SuperCam offers very similar capabilities, but SuperCam passive sky data processing is much less mature.

For the present work, we now incorporate MSL Alpha Particle X-ray Spectrometer (APXS) measurement of the atmospheric argon column [9] to allow us to distinguish chemistry-driven $O₂$ variability from the effects of atmospheric dynamics combined with the $CO₂$ condensation/sublimation cycle that perturb the mixing ratios of all non-condensable gases. Although APXS offers only a relative rather than absolute measurement of Ar, unlike SAM it provides measurements at a sampling periodicity comparable to that of ChemCam passive sky.

Results: Figure 1 shows mixing ratios for ChemCam O2, SuperCam O2, ChemCam water vapor, and APXS Ar multiplied by an arbitrary scale factor. We have focused on Mars Year 37 here because it has not been presented previously, and because starting roughly

Figure 1. Volume mixing ratios of ChemCam O2 (black), SuperCam O2 (grey), ChemCam water vapor (green), and APXS argon (blue), for Mars Year 37. Data after Ls = 145° *in Mars Year 37 is not yet publicly released.*

at the beginning of Mars Year 37 nearly all ChemCam passive sky measurement were accompanied by an APXS argon measurement on the same or adjacent sol, and because Mars Year 37 to date offers a particularly clear example of apparently chemistry-driven O_2 variability.

ChemCam O2 clearly grows much more rapidly after $L_s = 90$ than do non-chemically-active trace gases as represented by argon, and it does so in the same season that SAM has reported most of its observed anomalous rapid increases in O_2 [1]. Not all Mars years of ChemCam O2 measurements show this particular pattern of deviation from argon, but in none does $O₂$ match the seasonal pattern of argon. SuperCam O_2 in Mars Year 37 has a great deal of scatter compared to ChemCam O2 in Mars Year 37, but *average* SuperCam O2 is consistent with the *average* ChemCam O2 abundance of 2000 ± 60 ppm [7] and SuperCam O_2 also seems consistent with the same rapid $L_s = 90^\circ - 150^\circ$ seasonal rise that ChemCam sees in Mars Year 37. We presume that the excess scatter in SuperCam $O₂$ is due to the less mature data processing, but this is a question that we are actively investigating. Lastly, while the ChemCam-measured water vapor column shows no particular correlation with $O₂$ for the first 90 degrees of L_s in this year, once the rapid seasonal rise of $O₂$ arrives the water vapor and O_2 are strongly correlated.

Discussion: The correlation between O₂ and water vapor during the season when both are rising rapidly suggests that the excess $O₂$ variability may have a source region in common with the well-known seasonal rise in water vapor. This in turn implies some kind of association with sublimating seasonal water ice during northern summer, but it is important to note that trends in both water vapor and $O₂$ during northern summer show substantial inter-annual variability. Note also that no corresponding southern summer seasonal rise in either O₂ or H₂O has ever been observed by MSL, even though high southern latitudes certainly experience summer-season elevated water vapor from sublimation [e.g. 10]. This highlights the fact that the observed seasonal variability in both O_2 and H_2O in the tropics has as much to do with transport as it does with the physical processes the cause those species to be released in the atmosphere.

Consistent with the suggestion in [11] that the atmosphere provides the source of O atoms for perchlorate formation, both [1] and [2] suggest soil oxychlorines as a candidate non-atmospheric reservoir for the O atoms that seem to have interannually variable seasonal exchanges with the atmosphere. Water vapor has been suggested to be critically important for enabling that exchange [2, 12], and the Viking gas

exchange experiments showed release of oxygen from soil upon humidification Klein, 1978; Oyama & Berdahl, 1977). Thus the high concentration of water vapor provided by seasonal water ice sublimation may be responsible for the observed correlation between excess O_2 and water vapor. However UV flux is also important the degradation of perchlorates [12] so we should expect to also find other correlations related to UV flux and hence atmospheric opacity. UV flux correlations will of course be complicated by transport processes just as the water vapor correlations are.

References:

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