Organic chemistry influences the observed seasonal cycle of molecular oxygen on Mars

Benjamin M. Taysum,[1,2]* Paul I. Palmer,[1,2]

[1]School of GeoSciences, University of Edinburgh, Edinburgh, UK
[2]Centre for Exoplanet Science, University of Edinburgh, Edinburgh, UK

*To whom correspondence should be addressed; E-mail:Ben.Taysum@ed.ac.uk.

Recent measurements collected by the Mars Curiosity Rover at the Gale Crater revealed an unexpectedly large seasonal cycle of molecular oxygen (O_2). We use a 1-D photochemical model, including inorganic and organic chemistry, and its adjoint model to quantify the sensitivity of changes in O_2 to changes in inorganic and organic compounds. We show that O_2 changes are most sensitive to changes in organic compounds from the oxidation of methane. We find that an accelerated loss of atmospheric methane, achieved either by increasing the atmospheric loss or by imposing an additional surface loss, does not reconcile model and observed values of O_2 but it helps to explain the O_2 seasonal variation. The resulting changes in atmospheric composition are below the detection limits of orbiting instruments.

Atmospheric observations of methane (CH_4) on Mars, often considered an indicator of microbial life, have long since been a source of curiosity and controversy. Over the past two decades, CH_4 observations have been reported by orbiting satellites (*1–3*), ground-based telescopes (*4–6*), and by *in situ* measurements at Gale Crater by the Curiosity Rover (*7*). A five-

1

year analysis of Curiosity CH_4 measurements from the Sample Analysis at Mars (SAM) suite revealed variations indicative of a seasonal cycle (*8*), but more data are needed to confirm this cycle (*9*). However, other data, including recent orbiting instruments, have failed to detect atmospheric CH_4 (*10,11*). Observed variations of CH_4, from the Curiosity Rover team or collectively via the range of measurements, are arguably more unexpected than the presence of CH_4. They would suggest, for example, an atmospheric loss process that is faster than known atmospheric chemistry or an unrealistic population of surface methanotrophic organisms. Either scenario potentially overwhelms the atmospheric redox budget (*12*).

Atmospheric photochemical models of Mars estimate the photochemical lifetime of CH_4 to be >250 years below altitudes 70 km (*13–16*). Given characteristic atmospheric transport timescales, this photochemical lifetime suggests that Martian CH_4 should be well-mixed throughout the atmosphere. Reconciling models and data either requires an atmospheric loss process that corresponds to a lifetime shorter than 200 days (*13, 16*) or a lifetime of the order of one hour against a surface loss process. The known atmospheric losses below 70 km for CH_4 are oxidation by atomic oxygen ($O(^3P)$, $O(^1D)$) and the hydroxyl radical (OH), resulting in the production of methyl and methoxy radicals (CH_3, CH_3O). Recent analysis of molecular oxygen (O_2) measurements from the tunable diode laser aboard the SAM at Gale Crater revealed an unexpectedly large seasonal variation of O_2 (*17*) that cannot be reproduced by current photochemical models. During the Northern hemisphere's Autumn and Winter periods, observed values of O_2 decreased by 23% over a 38-sol period, consistent with a lifetime of approximately 150 days which is much shorter its expected photochemical lifetime of 10 years (*18*). Knowledge of O_2 photochemistry can not currently be reconciled with observed variations in O_2. Limitations to current knowledge of the chemical and physical properties of Martian soil precludes any definite explanation for observed variations of O_2. Consequently, the current suite of Martian CH_4 and O_2 measurements present a conundrum: can we reconcile observed

variations of CH_4 and O_2, related by photochemistry, without overwhelming the atmospheric redox chain?

Here, we use a 1-D atmospheric photochemistry model of Mars (*16*) to study the influence of reactive inorganic and organic gas-phase chemistry on CH_4 and O_2 and to interpret observed SAM measurements of O_2. To achieve this, we calculate the tangent linear model (TLM) and its adjoint of the 1-D model, both common approaches to study the physics and chemistry of Earth's atmosphere (*19, 20*). The TLM describes the first derivative of the time-dependent photochemical model, e.g. what is the sensitivity of O_2 to a change in trace gas A? A more elegant approach is to use the adjoint of the TLM that allows us to ask the question: which inorganic and organic trace gases are responsible for an observed change in O_2? The 1-D photochemical model, with vertical resolutions ranging from 10–100 m below 1 km and 1–10 km up to an altitude of approximately 70 km, uses pre-calculated half-hourly values for physical atmospheric parameters such as surface pressure, temperature, wind, and turbulent kinetic energy profiles from the Mars Climate Database v5.3 (MCDv5.3) (*21*), interpolated to the location of Gale Crater (4.5° S, 137.4° E). We also initialise the model with mixing ratio profiles of CO_2, CO, O_2, H_2O vapour, and H_2 from the MCDv5.3 dataset, and with a uniform profile of 50 ppt of CH_4 which is consistent with current observations (*11*). For each solar longitude (L_s) we report, we spin-up the model over 110 sols to generate steady-state values for longer-lived chemical species, e.g. H_2O_2, formaldehyde (HCHO), and methy hydroperoxide (CH_3OOH). We then run the TLM and its adjoint model over three successive sols and report those results.

Figure 1a,b shows the sensitivity of surface O_2 VMR at Gale Crater to changes in O_3, H_2O vapour, H_2O_2 and H_2, and to changes in CH_4 and a subset of its oxidation products (HCHO, CH_3OOH, and CH_3OH). With the exception of O_3, we find that O_2 is negatively sensitive to changes in inorganic and organic precursors, with peak values at or below 1 km as expected

given the two-sol time period. Sensitivities are generally largest at L_S=133° when the water vapour content in the column above Gale Crate (4.5° South, 137.4° East) reaches its seasonal maximum. This also coincides with the time at which the optical opacity of the Martian atmosphere (determined primarily by dust) is at its lowest, prior to the seasonal rise occurring at a solar longitude of approximately 145° (*22*).

Generally, we find that surface O_2 at Gale Crater is more sensitive to changes in HCHO and CH_3OOH, two key oxidation products of CH_4, than either H_2O_2 and water vapour. This sensitivity corresponds to an initial state with 50 ppt CH_4 (*11*). In comparison, the sensitivity of O_2 to changes in CH_4 using our control chemical network (*16*) is much smaller due to its longer chemical lifetime that exceeds 200 years (*16*). The large sensitivity of O_2 to changes in CH_4 oxidation products, coupled with the need for a faster CH_4 (physical, chemical, or biological) loss process to reconcile with Rover CH_4 measurements (*13*), leads us to examine how O_2 would respond to an accelerated loss process close to the Martian surface. To investigate this we force atmospheric CH_4 to have a lifetime of one hour below 400 m. We accomplish this by including a reaction that splits CH_4 into atomic hydrogen and the CH_3 radical, mimicking the photolysis of CH_4 that is only efficient above 60 km and electrochemical reactions that could results from dust charging due to wind saltation, dust devils and dust storms (*23, 24*). We find that this accelerated (seasonally invariant) loss of CH_4 only affects the sensitivity of O_2 to changes in CH_4, as expected, which increases by four orders of magnitude ($O(10^{-1})$) at all solar longitudes. There is no route in the chemical network to recover CH_4 from its oxidation products so their relationship to O_2 remains the same. SAM has previously measured variations in CH_4 at Gale Crater of the magnitude 10^{-10}–10^{-9} mol/mol (*17*). Based on our sensitivity calculation, an increase of 10% in CH_4 would result in a decrease in O_2 of 10^{-11}–10^{-10} mol/mol. Our calculations suggest that surface O_2 is as sensitive to CH_4 released two sols prior as its inorganic precursors (Fig. 1a). Our results also suggest that a large surface loss for

4

CH$_4$, which would reconcile photochemical models with measurements, would have significant implications for the seasonal cycle of O$_2$.

Figure 2 shows the relationship between the lifetime of atmospheric CH$_4$ and O$_2$ at Gale Crater. We initialise CH$_4$ in the first model layer in our calculations using measured season-specific values (*8*) (Fig. 2a). Using our approach to describe the accelerated CH$_4$ loss, we define the lifetime of CH$_4$ below 400 m from 15 mins to one week during daylight (solar zenith angle >95°) that reverts back to the standard chemical network in the absence of sunlight. Our spin-up period from these conditions is 110 sols, which is much longer than the vertical mixing timescale ($\simeq$ 2 sols). Fig. 2a shows the change in the CH$_4$ column loss below 400 m, which increases by several orders of magnitude from the control value of 10^3 molec cm^{-2} s^{-1} as the lifetime decreases. Fig. 2b shows that the corresponding column lifetime of O$_2$ in lowest 10 km is significantly decreased (> factor of three) by small (ppb) increases in CH$_4$ in the surface layer due to an accelerated surface loss process. The largest absolute change in O$_2$ lifetime is during northern spring (L$_S$ = 0–90°) when the SAM CH$_4$ values are highest (Fig. 2a) and the O$_2$ loss is largest (Fig. 2c), and the small absolute change is during northern summer (L$_S$ = 90–180°) when the O$_2$ loss is smallest (Fig. 2c). Fig. 2d shows observed surface O$_2$ values at Gale Crater measured by SAM (*17*), and the steady-state O$_2$ values at noon (local time of 12:00) at the surface as calculated by the 1-D chemistry model, defined as the ratio of the photochemical production of O$_2$ (molec cm^{-3} s^{-1}) and the photochemical loss of O$_2$ (s^{-1}), normalised by atmospheric number density to convert to VMR units. We acknowledge this approach is an approximation because of the long lifetime of O$_2$ and our inability using our 1-D model to properly describe deviations from zonal mean transport, but our method does provide some indication of how changes in CH$_4$ chemistry will impact O$_2$. We find that an accelerated organic chemistry network cannot explain the additional O$_2$ needed to reconcile with the SAM observations. We find that an O$_2$ lifetime of $\simeq$1000 sols is required to reconcile our photochemical

5

model with SAM O_2 observations at L_S=140° in Mars Year 33 (*17*), corresponding to a CH_4 loss of $>10^{10}$ molecules cm^{-2} s^{-1}. This CH_4 loss rate is unachievable with the SAM CH_4 observations, irrespective of the CH_4 lifetime we prescribe. Achieving this loss flux of CH_4 would require a larger ppb-level abundance of CH_4.

Figure 3 compares the SAM and photochemical model O_2 values at Gale Crater, corresponding to Fig. 2d, but with values normalized by the corresponding observed or model value at $L_S = 345°$ We find that the best agreement between seasonal model and measured O_2 values, using SAM measured CH_4 VMRs at the surface (*7*), corresponds to a CH_4 lifetime shorter than two hours during $L_S = 0–75°$, increasing to 2–12 hours during $L_S = 75–135°$, before decreasing to less than two hours during $L_S = 135–360°$. These changes to the chemical network result in better agreement with the observed O_2 seasonal cycle, relative to our control run, during solar longitudes $90° – 180°$. An additional requirement to reconcile SAM measurements with photochemistry models is the addition of 10^{20} O_2 molecules cm^{-2} to the column between L_S 60–140° (*17*). We find that the accelerated organic chemistry network cannot increase the rate at which O_2 is produced and therefore cannot be responsible for this additional O_2 that is missing from current photochemical models (Fig. 2d). A speculative scenario that would help reconcile the magnitude and seasonal variation of photochemical model and the SAM O_2 observations is a seasonally-varying CH_4 loss process that peaks during the dusty season when optical opacity is highest ($L_S = 150–10°$, Fig. 3b) that would suppress the net production of O_2 from additional seasonally-invariant near-surface source. During periods when the optical opacity is at a minimum, i.e. outside the dust season, the combination of an active O_2 source and a lower rate of destruction for CH_4 could result in an additional $10^{17}–10^{18}$ molecules cm^{-2} sol^{-1} that would accumulate to 10^{20} O_2 molecules cm^{-2} within 100 sols. Previous laboratory studies have proposed mechanisms that would allow dust to remove CH_4 from the atmosphere (*25–27*), but there is still a great deal that we do not understand about airborne dust on Mars.

An accelerated organic chemistry network would also increase the production of trace gases that are observable from the Trace Gas Orbiter. Formaldehyde, for example, would be present at 0.1–1 ppb levels below 2 km, exceeding the instrument detection limits for the Atmospheric Chemistry Suite during low dust periods (0.17 ppb) but not during high dust periods (1.7 ppb) (*28*). The Nadir and Occultation for MArs Discovery instrument is capable of detecting 0.03 ppb of HCHO during solar occultations with a signal-to-noise ratio of 3000 (*29*), which the model predicts at altitudes of 2.5–4 km, a region that is difficult to observe using solar occultation because of dust along the observed limb. If the accelerated network was driven exclusively by a surface loss process, the resulting CH_4 and O_2 perturbations would be mainly limited to the lowest 5 kms and would likely evade detection by satellite observations thereby reconciling results from recent satellite and *in situ* measurements.

Altering the speed at which photochemistry takes place on Mars will have implications of the redox budget (*12*), which demands a balance with our new source of oxidising power that is ten times stronger than is available with current knowledge. We also have to consider that the discrepancy between SAM O_2 observations and our standard photochemical model reflects an unknown physical or chemical process that is unrelated to CH_4 (*17*), and that the similar seasonal cycles are a coincidence. If this uncharacterized physical or chemical process acts as a source of O_2 then the accelerated CH_4 chemical network close to the Martian surface coupled with said process could help in coinciding the true O_2 VMRs measured by SAM and the strength of the O_2 cycle at Gale Crater, and these missing sources may act as a source for the redox budget balancing required for the chemical loss of CH_4. Although several Martian surface loss processes for CH_4 have been proposed (*26, 27, 30*), we have taken a process-agnostic approach by prescribing the resulting change in CH_4 lifetime. The presence of perchlorates (ClO_4^-) within the Martian soil (*31*) is a possible surface source for O_2 at Gale Crater via radiolysis (*32*). However, radiation levels at the Martian surface are insufficient to reproduce observed O_2 values

and this proposed O_2 source would need to be accompanied by fluxes of hydrogen and chlorine which have not been observed on Mars to date. Regolith diffusion of atmospheric H_2O_2 has also been proposed to emit surface O_2 (*33*). Atmospheric H_2O_2 is present in the Martian atmosphere at ppb levels (*34*) so the production rate of O_2 would have to be exceptionally fast.

Our calculations not only show that organic chemistry has a role to play in understanding changes in O_2 but also a better understanding of Martian soil and dust could potentially play a key role in helping to reconcile observed changes in CH_4 and O_2. Data from instruments aboard the recently landed NASA Perseverance Rover will provide valuable data regarding the geology and surface at Jezero Crater (*35*). The Mars Environmental Dynamics Analyzer (*36*) aboard Persevereance aims to further study and parameterize Martian dust size and shapes, vital for the modelling of gas-particle heterogeneous chemistry, and numerous instruments aboard aim to study the mineralogy of the surface which will provide greater understandings of possible atmosphere-surface interactions.

References

1. V. Formisano, S. Atreya, T. Encrenaz, N. Ignatiev, M. Giuranna, *Science* **306**, 1758 (2004).

2. A. Geminale, V. Formisano, M. Giuranna, *Planetary and Space Science* **56**, 1194 (2008).

3. M. Giuranna, *et al.*, *Nature Geoscience* (2019).

4. V. A. Krasnopolsky, J. P. Maillard, T. C. Owen, *Icarus* **172**, 537 (2004).

5. M. J. Mumma, *et al.*, *Science* **323**, 1041 (2009).

6. G. Villanueva, *et al.*, *Icarus* **223**, 11 (2013).

7. C. R. Webster, *et al.*, *Science* **347**, 415 (2015).

8. C. R. Webster, *et al.*, *Science* **360**, 1093 (2018).

9. E. Gillen, P. B. Rimmer, D. C. Catling, *Icarus* **336**, 113407 (2020).

10. V. A. Krasnopolsky, *Icarus* **217**, 144 (2012).

11. O. Korablev, *et al.*, *Nature* **568**, 517 (2019).

12. K. Zahnle, R. S. Freedman, D. C. Catling, *Icarus* **212**, 493 (2011).

13. F. Lefèvre, F. Forget, *Nature* **460**, 720 (2009).

14. A. S. Wong, S. K. Atreya, *Advances in Space Research* **33**, 2236 (2004). Mercury, Mars and Saturn.

15. A.-S. Wong, S. K. Atreya, T. Encrenaz, *Journal of Geophysical Research: Planets* **108** (2003).

16. B. M. Taysum, P. I. Palmer, *Journal of Geophysical Research: Planets* **125**, e2020JE006491 (2020).

17. M. G. Trainer, *et al.*, *Journal of Geophysical Research: Planets* **124**, 3000 (2019).

18. S. Atreya, Z. Gu, *Advances in Space Research* **16**, 57 (1995). The Atmospheres of Venus and Mars.

19. R. M. Errico, T. VukiEvi, K. Raeder, *Tellus A: Dynamic Meteorology and Oceanography* **45**, 462 (1993).

20. S. Frolov, *et al.*, *Monthly Weather Review* **146**, 2247 (2018).

21. E. Millour, *et al.*, *EGU General Assembly Conference Abstracts* (2017), vol. 19 of *EGU General Assembly Conference Abstracts*, p. 12247.

22. M. T. Lemmon, *et al.*, *Icarus* **251**, 96 (2015). Dynamic Mars.

23. T. L. Jackson, W. M. Farrell, G. T. Delory, J. Nithianandam, *Journal of Geophysical Research: Planets* **115** (2010).

24. J. F. Kok, N. O. Renno, *Geophysical Research Letters* **36** (2009).

25. S. J. Knak Jensen, *et al.*, *Icarus* **236**, 24 (2014).

26. R. Gough, *et al.*, *Planetary and Space Science* **59**, 238 (2011). Methane on Mars: Current Observations, Interpretation and Future Plans.

27. H. J. Jakobsen, *et al.*, *The Journal of Physical Chemistry C* **120**, 26138 (2016).

28. O. Korablev, *et al.*, *Space Sci. Rev.* **214**, 7 (2018).

29. A. C. Vandaele, *et al.*, *Space Sci. Rev.* **214**, 80 (2018).

30. S. K. Atreya, P. R. Mahaffy, A.-S. Wong, *Planetary and Space Science* **55**, 358 (2007). Planet Mars II.

31. B. Sutter, *et al.*, *Journal of Geophysical Research: Planets* **122**, 2574 (2017).

32. R. C. Quinn, *et al.*, *Astrobiology* **13**, 515 (2013). PMID: 23746165.

33. J. Lasne, *et al.*, *Astrobiology* **16**, 977 (2016). PMID: 27925795.

34. Encrenaz, T., *et al.*, *A&A* **578**, A127 (2015).

35. K. A. Farley, *et al.*, *Space Sci. Rev.* **216**, 142 (2020).

36. J. A. Rodriguez-Manfredi, *et al.*, *3rd International Workshop on Instrumentation for Planetary Mission* (2016), vol. 1980, p. 4114.

37. M. D. Smith, M.-P. Zorzano, M. Lemmon, J. Martn-Torres, T. Mendaza de Cal, *Icarus* **280**, 234 (2016). MicroMars to MegaMars.

Acknowledgments

Supplementary materials

Materials and Methods

Supplementary Text

Figs. S1 to S4

References

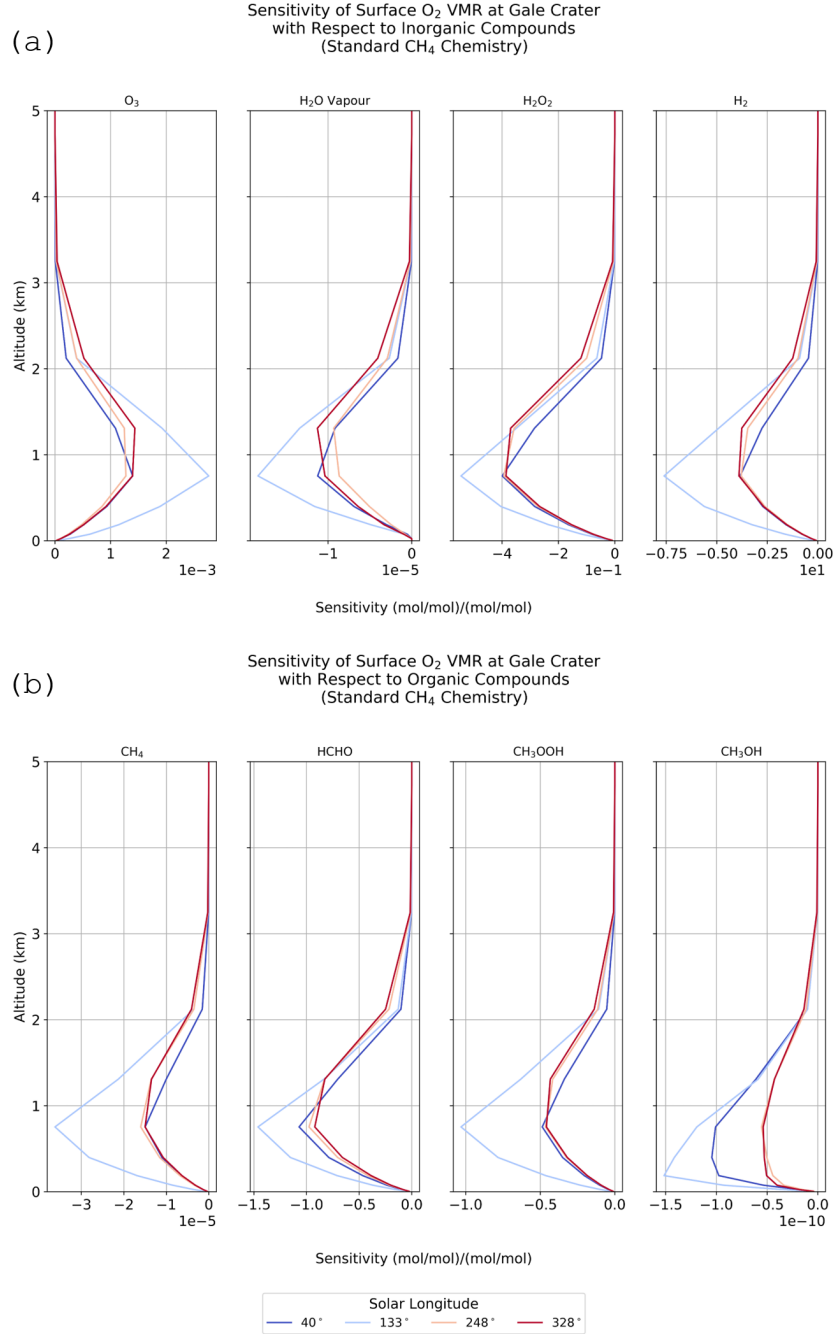Figure 1: Sensitivity ((mol/mol)/(mol/mol)) of surface O_2 volume mixing ratios at Gale Crater to changes in a) inorganic (O_3, H_2O vapour, H_2O_2 and H_2) and b) organic (CH_4, HCHO, CH_3OOH, and CH_3OH) compounds within our control photochemical model. All calculations are reported at a local time of 00:00, and initialised uniformly with 50 ppt of CH_4 two sols prior at local noon. Different lines denote calculations evaluated at various solar longitudes along the seasonal cycle: 40°, 122°, 248°, and 328°.
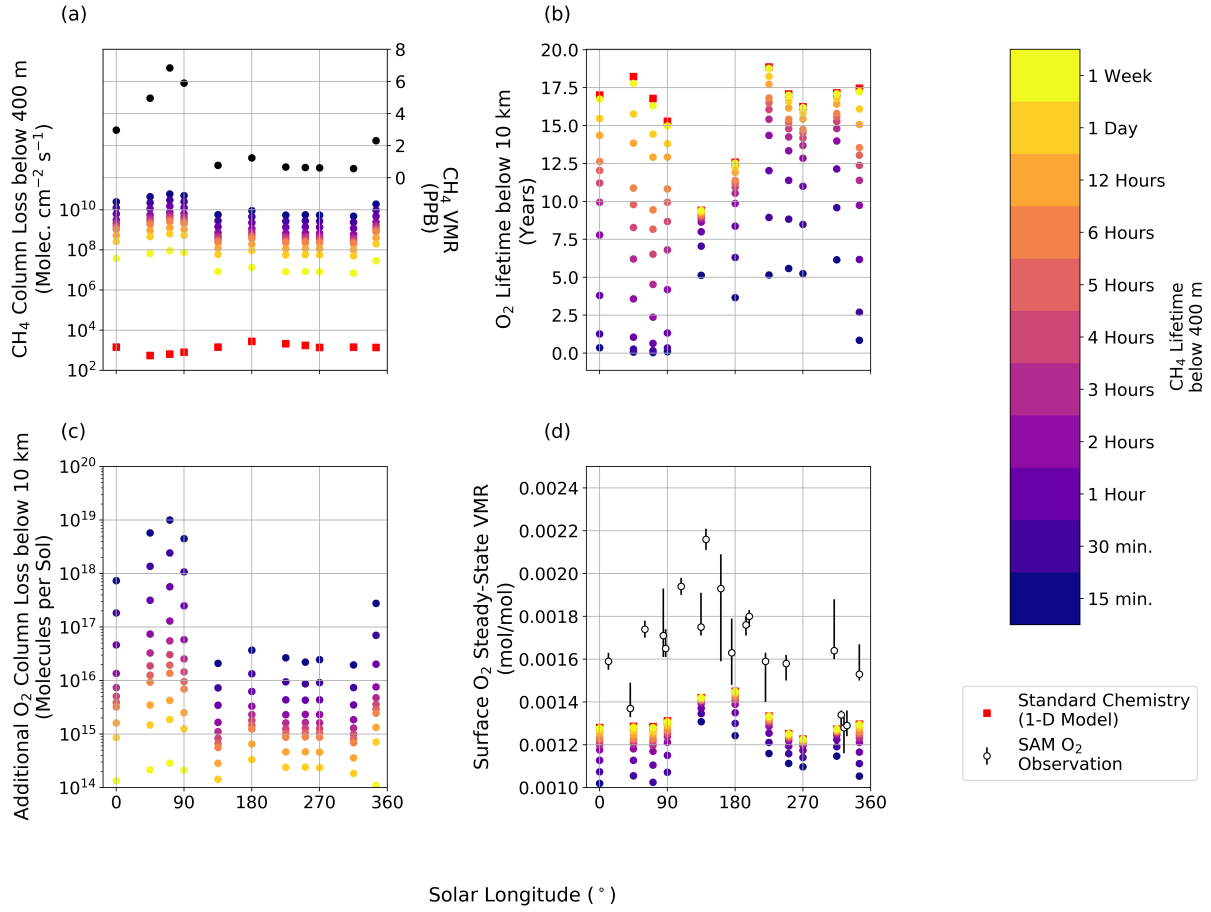
13

Figure 2: The impacts of including an accelerated photochemical surface sink for CH_4 on O_2 at Gale Crater on the a) O_2 chemical lifetime (years) below 10 km; (b) loss flux of CH_4 below 400 m (molecules cm^{-2} s^{-1}) that is influenced by prescribing the observed seasonal cycle of CH_4 VMR during MY 32–33 (8); (c) additional O_2 loss below 10 km per sol (molecules sol^{-1}); and (d) observed and model steady-state O_2 VMRs at the surface of Gale Crater.
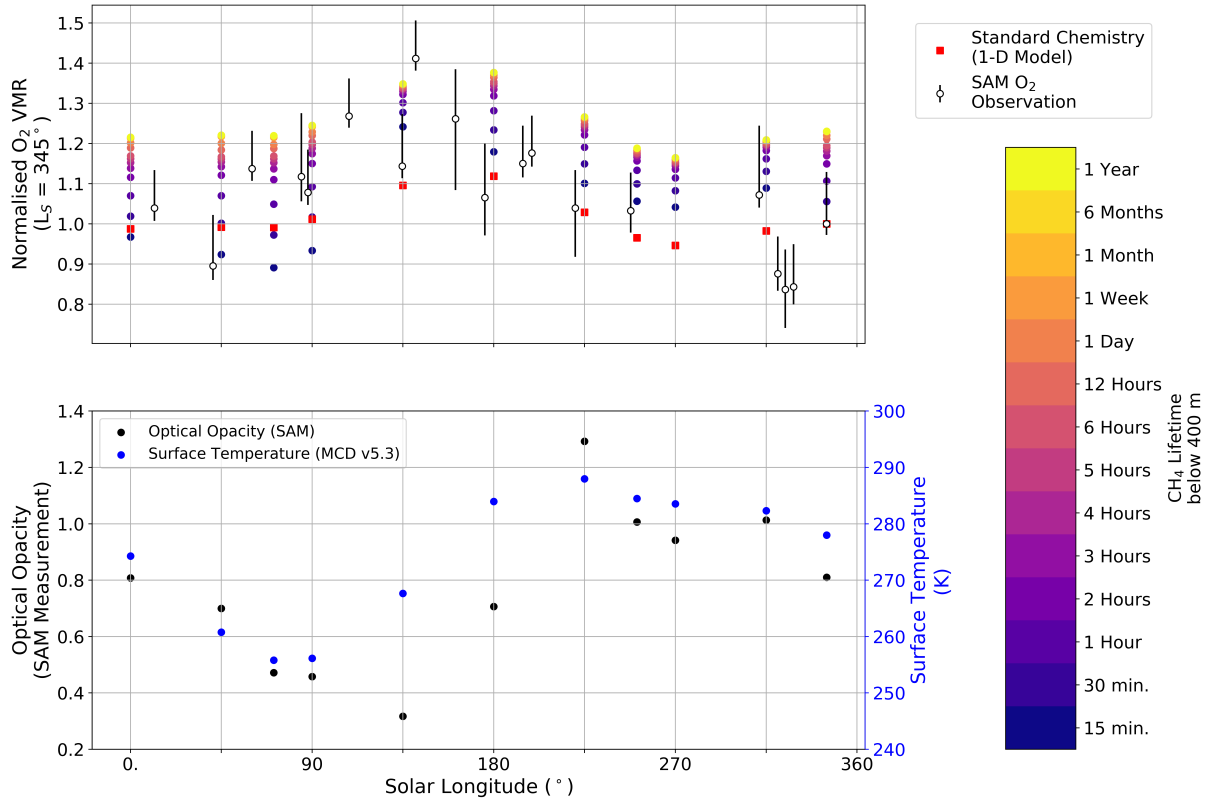
Figure 3: (a) Observed and model seasonal cycle of O_2 at the surface of Gale Crater, normalized by observed and model values at $L_S = 345°$. Model values correspond to the standard photochemical network and to the network that corresponds to a prescribed CH_4 lifetime below 400 m. (b) Observed optical opacity from MY 32–33 (*37*) and model surface temperature (K) (*21*).