Methane on Mars from MSL-Curiosity and ExoMars-Trace Gas Orbiter: A Destructive Role of Surface Oxidants? Sushil K. Atreya[1], Thérèse Encrenaz[2], Oleg Korablev[3], Paul R. Mahaffy[4], John E. Moores[5], Ann C. Vandaele[6], Christopher R. Webster[7], Pierre-Yves Meslin[8], Rafael Navarro-Gonzalez[9], [1]Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI 48109-2143 USA (atreya@umich.edu), [2]LESIA, Observatoire de Paris, PSL, 92195 Meudon, France (therese.encrenaz@obspm.fr), [3]Space Research Institute (IKI), Russian Academy of Sciences, Moscow, Russia (olegkorab@gmail.com), [4]NASA Goddard Space Flight Center, Greenbelt, MD 20771 (paul.r.mahaffy@nasa.gov), [5]Centre for Research in Earth and Space Science, York University, Toronto, ON M3J 1P3, Canada (jmoores@yorku.ca), [6]Royal Belgian Institute for Space Aeronomy, Brussels, Belgium (a-c.vandaele@aeronomie.be), [6]Caltech Jet Propulsion Laboratory, Pasadena (chris.r.webster@jpl.nasa.gov), CA 91109 USA, [8]Institut de Recherche en Astrophysique et Planétologie, Toulouse, France (pmeslin@irap.omp.eu), [9]Universidad Nacional Autonoma de Mexico, Ciudad de Mexico 04510, Mexico (navarro@nucleares.unam.mx).

Introduction: Being a potential biosignature, detection of methane on Mars has been pursued vigorously. There is an apparent discrepancy between the newly acquired TGO data, which show no methane on Mars, and seven years of MSL data, which show a low background level of methane and occasional spikes. Here we discuss the potential role of surface oxidants to reconcile the difference. In particular, we propose a hypothesis of fast destruction of methane *near the surface* of Mars.

Methane by MSL: The Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars suite (SAM) on the Curiosity Rover of the Mars Science Laboratory (MSL) has carried out in situ measurements of methane at the surface of Mars since the rover landed in Gale Crater in August 2012 [1,2]. Initially, measurements were done by directly ingesting Mars air. A cluster of 4 spikes averaging 7 ppbv was detected within a period of 2 months from November 2013 to January 2014, and a lone spike of about the same magnitude was recorded four months earlier on 16 June 2013, which was absent when the next observation was done a week later. As no measurements were done over the 4-month span between the June spike and the set of 4 spikes starting November 2013, we cannot be certain whether spikes came and went during that time. Using a spot-tracking mode and by binning hundreds of spectra, Planetary Fourier spectrometer (PFS) on Mars Express confirmed the 16 June 2013 spike recorded previously by TLS-SAM [3]. PFS did not observe Gale during times of other spikes recorded by MSL. Beginning in March 2014, the Mars air sample delivered to the TLS was pre-enriched in methane by SAM that scrubbed CO_2 and H_2O from the sample, but not CH_4, resulting in a factor of ~25 increase in the methane abundance analyzed by the TLS. These data yield a precise measurement of methane, which shows a low background level of methane at Gale Crater, averaging 0.41 ± 0.16 ppbv, and showing a strong seasonal variation ranging from 0.24 to 0.65 ppbv.

Methane by ExoMars: The ACS and NOMAD instruments onboard ESA's ExoMars Trace Gas Orbiter (TGO) have searched for methane on Mars using a highly-sensitive solar occultation mode. The early results from April to August 2018 detect no methane, giving an upper limit of 0.05 ppbv [4], which is at least a factor of ten lower than the MSL result. The best results from TGO are above 5 km altitude and in high northern latitudes. Because of the constraints of solar occultation geometry, observations covering Gale Crater are not yet available. Nevertheless, it appears there is a discrepancy between the TGO and MSL results on methane.

ExoMars-MSL Methane Dilemma: At first glance, it could be argued that since TGO and MSL are sampling two different altitude regimes, and in different locales, differences between their methane results can be a real possibility. However, when one considers that the time for vertical mixing can be as short as 1 day (and up to 10 days, depending on the strength of vertical mixing), TGO should be detecting approximately similar abundance of methane as MSL detects at the surface. It would be especially true if there are distributed sources of methane like Gale Crater scattered all over Mars, considering that meridional mixing would spread methane over the planet in about 3 months, and the photochemical equilibrium lifetime of methane in the atmosphere of Mars is about 350 years [5]. That poses a dilemma – how to reconcile the MSL and TGO results.

Surface Oxidants to Reconcile the Methane Dilemma: A plausible scenario involves rapid removal of methane *near the surface* of Mars. The mechanism does not operate on Earth, nor is it expected to, allowing atmospheric photochemistry alone to control the 10-year lifetime of methane in the Earth's atmosphere. Laboratory experiments relevant to Mars have previously suggested methane can be sequestered in activated quartz grains produced by wind erosion process [6], but it is not evident whether it is a temporary storage and whether the process can be efficient close to the surface of Mars, where the average winds speeds (few m/s) are relatively low. On the other hand, chemical removal of methane near the surface is a real possibil-

ity. Hydrogen peroxide (H_2O_2) and perchlorates ($ClO4^-$) are potent oxidants implicated in the destruction of surface organics on Mars. They could also destroy atmospheric methane. Loss of methane by "chlorine" from perchlorates would result in chlorine-bearing molecules in the atmosphere, which have not been detected even at 0.1 ppbv levels. Though H_2O_2 does not directly destroy methane, highly reactive superoxides resulting from it such as HO_2 and O_2^- can [7,8]. Instruments to detect H_2O_2 in the surface/regolith of Mars have not yet flown, but it is expected to be present there. Low levels of H_2O_2 up to 40 ppbv have been detected in the atmosphere of Mars [9]. Moreover, electrochemistry models predict large production of H_2O_2 by triboelectric process in convective dust events on Mars [7,10], and laboratory experiments confirm the validity of the process [11]. Upon diffusion into the regolith, the H_2O_2 concentration would build up [12]. Subsequent mineral reactions and radiolysis ground-penetrating galactic cosmic rays are expected to produce abovementioned superoxides from H_2O_2.

It has been suggested previously that any methane produced by biology or geology on Mars may be stored in subsurface reservoirs as clathrates [13]. When that methane is released, the same process is likely to trigger the release of oxidants and associated products including superoxides along with it. The ensuing fast reactions would result in a rapid destruction of methane close to the surface, before it has a chance to mix vertically and globally. Thus, the low background level of methane detected by SAM's TLS instrument suggests a continuous source associated with continuous removal of methane at a rapid rate. As the proposed destruction of methane on oxidants takes place near surface, TGO may not detect the methane that MSL records at the surface.

Caveats and Future Work: Finally, it important to remember that it is too soon to conclude from the limited set of TGO observations over only a fraction of one Mars year that there is no methane anywhere, anytime on Mars. Should TGO detect large concentrations of methane sometime in the future, the above mechanism of loss of methane on oxidants near the surface may be slow to act. The oxidant hypothesis presented here would greatly benefit from relevant laboratory simulations, and measurements of H_2O_2 and superoxides in the surface/regolith as well as atmospheric electric fields on future Mars missions.

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