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1 **Comprehensive Investigation of Mars Methane and Organics with**
2 **ExoMars/NOMAD**

3

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1 **Abstract**

2 Methane (CH₄) on Mars has attracted a great deal of attention since it was first detected in
3 January 2003. As methane is considered a potential marker for past/present biological or
4 geological activity, any possible detection would require evidence with strong statistical
5 significance. Ethane (C₂H₆) and ethylene (C₂H₄) are also relevant chemical species as their
6 shorter lifetimes in the Martian atmosphere make them excellent tracers for recent and ongoing
7 releases. If detected, a CH₄/C₂H_n ratio could aid in constraining the potential source of organic
8 production. Here we present the results of an extensive search for hydrocarbons in the Martian
9 atmosphere in 240,000 solar occultation measurements performed by the ExoMars Trace Gas
10 Orbiter/NOMAD instrument from April 2018 to April 2019. The observations are global,
11 covering all longitudes and latitudes from 85°N to 85°S, and sampled from 6-100 km altitude
12 with a typical vertical resolution of 2 km. There were no statistically significant detections of
13 organics and new stringent upper limits for global ethane and ethylene were set at 0.1 ppbv and
14 0.7 ppbv, respectively. No global background level of methane was observed, obtaining an
15 upper limit of 0.06 ppbv, in agreement with early results from ExoMars (Korablev et al., 2019).
16 Dedicated searches for localized plumes at more than 2000 locations provided no positive
17 detections, implying that if methane were released in strong and rapid events, the process would
18 have to be sporadic.

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1 **1. Introduction**

2 Mars has been characterized with ground-based observatories, Earth-orbiting
3 telescopes, Mars orbiters, landers and rovers with increasing intensity since the pioneering
4 studies of Mariner 4 in the mid 1960s. The ESA-Roscosmos spacecraft ExoMars Trace Gas
5 Orbiter (TGO) is the first mission dedicated to measuring the vertical distribution of
6 atmospheric trace gas composition on Mars (Vandaele et al., 2018). The Nadir and Occultation
7 for MArS Discovery (NOMAD) instrument is part of the remote sensing suite of TGO,
8 designed to observe the atmosphere in solar occultation, nadir and limb geometries to detect
9 minor gaseous species (e.g., CH₄, H₂O, CO, O₃, HCl) and their isotopologues. Determining the
10 abundance or existence of methane and other organics would improve current photochemical
11 models and provide novel insights into the astrobiological evolution of the planet (e.g. Atreya
12 and Gu (1995)).

13 The atmosphere of Mars is heavily oxidized and primarily composed of CO₂ (95.3%),
14 N₂ (2.7%) and Ar (1.6%), with modest amounts of O₂ and water vapor (Mangold et al., 2016).
15 Trace amounts of other noble gases are present (Ne, Kr, Xe), as well as molecular species such
16 as CO, O₃, NO and H₂O₂, which are produced photochemically from the primary volatiles
17 (Haberle et al., 2017). On Earth, atmospheric CH₄ is mostly produced by biological microbial
18 metabolism and anthropogenic processes, with the remainder being generated by geological
19 processes (Conrad, 2009). On Mars, CH₄ production by atmospheric chemistry is negligible,
20 implying that detections should be considered a signature of either biological or geological
21 activity (e.g., Krasnopolsky et al., (2004)). To date, a seasonally varying background level
22 (e.g., Geminale et al., (2011), Webster et al., (2018)) and short-lived localized plumes (e.g.,
23 Giuranna et al., (2019), Mumma et al., (2009), Webster et al., (2015)) have been reported.

24 The surface of Mars displays a wide variety of geological features, many of which date
25 back to the Noachian period (3.7-4.1 billion years ago) and strongly suggest liquid water once
26 flowed on the surface, potentially creating habitable conditions for microorganisms (e.g., Carr
27 (1996), Grotzinger et al., (2014)). If subsurface aqueous reservoirs exist on Mars today, they
28 may be able to sustain methanogenic organisms. On the other hand, potential sources of
29 methane do not necessarily need to be currently active: formerly produced CH₄ (of biotic or
30 abiotic origin) could be stored in clathrates for later release (Chastain and Chevrier, 2007).
31 Other potential sources of organics are impact metamorphism of already present or
32 meteorically delivered organics and thermogenesis of abiotic or biotic material (Oehler and
33 Etiope, 2017), and water-rock interactions (Etiope et al., 2013; Lyons, 2005). Furthermore,

1 exogenous sources such as in-fall of meteorites (Moores and Schuerger, 2012), and cometary
2 trails (Fries et al., 2016) have been posited. However, the latter process has been questioned as
3 other atmospheric consequences to such a mechanism have not been observed (Crismani et al.,
4 2017a; Roos-Serote et al., 2016).

5 The photochemical lifetime of CH₄ in the Martian atmosphere is estimated to be around
6 300 years while the global atmospheric mixing time is on the order of months (Krasnopolsky
7 et al., 2004; Lefèvre and Forget, 2009), implying that CH₄ is expected to be uniformly
8 distributed across the planet once a steady state is reached (Krasnopolsky, 2006; Summers et
9 al., 2002; Viscardy et al., 2016; Waugh et al., 2019). An enhanced level of CH₄ therefore
10 requires an active production or a release mechanism from ancient reservoirs. Without a strong
11 and rapid sink mechanism, CH₄ can potentially be detected long after its initial emission,
12 making it a poor tracker of ongoing activity. However, simulations suggest that if CH₄ is
13 detected shortly (<month) after being emitted from the surface, a highly nonuniform vertical
14 distribution is possible, including the formation of temporary layers (Viscardy et al., 2016). A
15 few weeks after release, the methane is expected to be uniformly mixed. Holmes et al., (2017)
16 showed that to distinguish between sustained and instantaneous surface emissions, at least ten
17 sols of monitoring the emission is necessary. In the same study, it was also found that to
18 distinguish direct surface release from atmospheric destabilization of methane clathrate
19 hydrates, the emission would need to be observed within ten sols of the initial release to avoid
20 it being incorrectly interpreted as a surface emission.

21 Ethane (C₂H₆) and ethylene (C₂H₄) have shorter photochemical lifetimes (25 years for
22 C₂H₆ (Wong, 2003), and around 1 day for C₂H₄), making them more suitable tracers of recent
23 and current activity if detected. C₂H₆ and C₂H₄ could also aid the degeneracy of potential
24 sources of methane on Mars. From experiments with lightning within volcanic plumes and
25 terrestrial analogs, some geological processes have been shown to release comparable amounts
26 of CH₄ and other hydrocarbons (CH₄/C₂H_n < 50), while biological activity generally produces
27 exclusively methane (CH₄/C₂H_n > 1000) (Bernard et al., 1977; Segura and Navarro-González,
28 2005). The presence of ethane and other high-n hydrocarbons in addition to methane is widely
29 accepted to distinguish geological from microbial origin for hydrocarbon gases, but the
30 CH₄/C₂H_n ratio cannot distinguish between ancient biogenic (thermogenic) processes and
31 abiogenic sources related to water-rock reactions (Allen et al., 2006). It must be mentioned that
32 processes could be mixed, and these ratios should not be used as conclusive evidence for
33 excluding either process.

1 1.1 Previous Searches for Methane on Mars

2 Before 2003, all searches for statistically significant methane were negative, or
3 consistent with no observed methane (Krasnopolsky et al., 1997; Lellouch et al., 2000;
4 Maguire, 1977). Since then, detections have been reported by four different groups (Mumma
5 et al., 2003, 2009; Krasnopolsky et al., 2004; Formisano et al., 2004; Webster et al., 2015;
6 Giuranna et al., 2019). Fonti and Marzo (2010) reported a methane detection with the Thermal
7 Emission Spectrometer onboard the Mars Global Surveyor, but during reanalysis the data
8 found the measurements could not unambiguously identify the presence of methane (Fonti et
9 al., 2015). Along with the groups reporting CH₄ detections, four independent searches yielded
10 no methane detections, but upper limits below 15 ppbv (Aoki et al., 2018; Korablev et al.,
11 2019; Krasnopolsky, 2007; Villanueva et al., 2013). Table 1 gives an overview of notable C₂H₆,
12 C₂H₄ and CH₄ searches reported since 2004.

Species	Abundance	Upper limit	Year of obs.	Reference
Ethane	–	0.2 ppbv ^b	2007	Krasnopolsky (2012)
Ethylene	–	4.1 ppb ^a	2006-2010	Villanueva et al., (2013)
Methane	10 ± 3 ppbv ^a	–	1999	Krasnopolsky et al., (2004)
	0 – 30 ppbv, localized ^c	–	2004	Formisano et al., (2004)
	(10 ± 5 ppbv, global) ^c	–		
	–	14 ppbv ^a	2006	Krasnopolsky (2007)
	5 – 61 ppbv, localized ^d	–	2004-2007	Geminale et al., (2008)
	(14 ± 5 ppbv, global) ^d	–		
	10 – 45 ppbv, plumes ^a	–	2003, 2006	Mumma et al., (2009)
	(3 ppbv, global) ^a	–		
	25 – 61 ppbv, localized ^d	–	2004-2009	Geminale et al., (2011)
	(15 ppbv, global) ^d	–		
	3 – 10 ppbv, localized ^b	8 ppbv ^b	2006, 2009	Krasnopolsky (2012)
	–	6.6 ppbv ^a	2006-2010	Villanueva et al., (2013)
5.5 – 9.3 ppbv, plume ^b	–	2012-2015	Webster et al., (2015)	
(0.69 ± 0.25 ppbv) ^b	–			
–	1 ppbv ^a	2016	Aoki et al., (2018)	
(0.41 ± 0.16 ppbv) ^b	–	2014-2017	Webster et al., (2018)	
15.5 ppbv, plume ^c	5 ppbv ^c	2013	Giuranna et al., (2019)	
–	0.05 ppbv ^b	2018	Korablev et al., (2019)	

13 ^a 3- σ uncertainty, ^b 2- σ uncertainty, ^c 1- σ uncertainty, ^d not specified.

1 **Table 1:** Currently most restrictive upper limits for ethane and ethylene, methane abundances
2 and upper limits below 15 ppbv reported since 2004. Global averages and background values
3 given in brackets.

4
5 The first reported detection of CH₄ was announced in 2003 (Mumma et al., 2003), and
6 later published in Mumma et al., (2009) after an intensive search in 2003 and 2006 using
7 several ground-based observatories. Shortly after the 2003 detection, Krasnopolsky et al.,
8 (2004) (utilizing a Fourier Transform Spectrometer at the ground-based Canada-France-
9 Hawaii Telescope) and Formisano et al., (2004) (using the Planetary Fourier Spectrometer
10 (PFS) on the Mars Express (MEX) satellite) reported comparable abundances. In 2007,
11 Krasnopolsky et al., (2007) reported a new upper limit, yet this value was not in conflict with
12 previously published detections. Geminale et al., (2011, 2008) used MEX/PFS to produce
13 temporal and spatial maps of CH₄ by averaging a large number of spectra. Mumma et al.,
14 (2009) reported a strong plume of CH₄ in 2003 that subsequently decreased rapidly by 2006.
15 Lefèvre and Forget (2009) pointed out that the destruction mechanism required to explain the
16 observations by Mumma et al., (2009, 2003), and the variations previously seen by
17 Formisano et al., (2004) and Geminale et al., (2008), are unexplained by known atmospheric
18 photochemistry and physical processes on Mars. It was suggested that the detections up to
19 that point should be considered tentative due to several limitations; low spectral resolution for
20 the MEX/PFS detections and the challenge of overlapping telluric and Martian lines for
21 ground-based detections (Encrenaz, 2008). Zahnle et al., (2011) went further, casting doubt
22 on all previous CH₄ detections and raising theoretical objections especially with regards to
23 methane variations. In addition to its challenge to conventional atmospheric chemistry,
24 variable CH₄ on the scale proposed would have major consequences for the Martian
25 atmosphere as a whole; if methane has an unknown chemical sink, it would be by far the
26 biggest term in the atmosphere's redox budget (Zahnle et al., 2011). It has also been implied
27 that analysis of previous obtained MEX/PFS nadir data might be erroneous, following the
28 spot-tracking technique applied by Giuranna et al., (2019). Until 2012, most reported
29 detections agreed on localized plumes (10-45 ppbv), with the possibility of local variations
30 and seasonal changes. Krasnopolsky et al., (2012) searched for CH₄ on two occasions; in
31 2006 and 2009, where the first dataset shows comparable amounts of methane to previous
32 studies, while the latter dataset found no trace of methane, obtaining an upper limit of 8 ppbv,
33 the lowest upper limit ever reported at that time.

1 The Mars Science Laboratory Curiosity Rover Tunable Laser Spectrometer
2 (MSL/TLS) has the purported capability of detecting CH₄ at pptv levels (Webster and Mahaffy,
3 2011). The first report on methane from MSL/TLS obtained the lowest upper limit so far of 1.3
4 ppbv (Webster et al., 2013), but the results were later revised and detections were reported with
5 an average background level of 0.69 ppbv using the enrichment process, and a plume of 7 ppbv
6 (Webster et al., 2015). This background abundance is lower than model estimates of ultraviolet
7 degradation of infalling interplanetary dust particles (IDP), however Schuerger and Moores
8 (2012) used IDP fluences from Flynn et al., (1996) which were an order of magnitude larger
9 than those recently observed by the Mars Atmosphere and Volatile Evolution Mission
10 (Crismani et al., 2017b; Grebowsky et al., 2017).

11 Villanueva et al., (2013) conducted an exhaustive search for organics in 2006, 2009 and
12 2010, using the VLT, Keck and IRTF observatories. This search yielded no detections of CH₄
13 or its oxidation products, and their upper limit of 6.6 ppbv for CH₄ was higher than the averaged
14 abundance (3 ppbv) for 2006 reported in Mumma et al., (2009). However, this non-detection
15 of CH₄ over Valles Marineris by Villanueva et al., (2013) twenty-eight days before the
16 detection by Krasnopolsky et al., (2012) was intriguing, as it may have suggested the presence
17 of large amounts of methane following a rapid release or production event (or issues with the
18 original detection). Aoki et al., (2018) performed sensitive searches for Martian CH₄ by using
19 the Echelon Cross-Echelle Spectrograph onboard the Stratospheric Observatory for Infrared
20 Astronomy, utilizing the high altitude of the instrument which significantly reduced the effects
21 of the terrestrial atmosphere; however, the results showed no unambiguous detections.

22 Webster et al., (2018) expanded on the results from Webster et al., (2015), adjusting the CH₄
23 background level once again to 0.41 ppbv, and their enrichment measurements at or near
24 midnight displayed a seasonal behavior. Moores et al., (2019a) suggested that the seasonal
25 variations are consistent with adsorption onto the regolith when combined with diffusion into
26 and out of the regolith, yet point out that the data can only be reconciled when assuming a
27 photochemical lifetime of CH₄ of 400 years in the hypothesis that Gale crater is the only
28 significant emission site on the planet. In addition, Gillen et al., (2020) conducted a statistical
29 analysis on the MSL/TLS dataset and found no evidence for a seasonal CH₄ cycle, stating that
30 the data are too sparse and cover a time span too limited to favor a seasonal period over
31 stochastic variations. The plume reported in Webster et al., (2015) was later reported as
32 confirmed by MEX/PFS (Giuranna et al., 2019) over Gale crater with a slightly higher
33 abundance of 15.5 ± 2.5 ppbv, one sol after the Curiosity detection. There were no detections
34 in any other orbital passages during a two-year period, with the reported upper limit ($1-\sigma$) set

1 to 5 ppbv. The results of Webster et al., (2015) have been questioned on the basis of potential
2 rover self-contamination (Zahnle, 2015), while other issues related to the enrichment factor
3 and increases in the methane amount present in the fore-optics were reported in Webster et al.,
4 (2018). Two recent papers (Olsen et al., 2020; Trokhimovskiy et al., 2020) identify and
5 quantify trace spectroscopic signatures of O₃ and a magnetic dipole CO₂ band in the 3.3 μm
6 spectral region, near features of the ν₃ band of CH₄. The features do not fully explain the MSL
7 results (Webster et al., 2020), they are relatively weak and do not completely overlap with the
8 methane lines, and therefore they cannot fully account for the reported abundance claims of
9 several ppbv of methane. However, their inclusion is important for improving systematics
10 removal and residual quality.

11 As summarized above, the detection of methane on Mars has a checkered past, with a
12 strong debate and conflicting claims. New sensitive measurements covering the whole planet
13 are therefore urgently needed. For this, the ExoMars TGO satellite is a highly valuable asset,
14 providing access to tens of ppt sensitivity limits since April 2018 when nominal science
15 operations began. Analysis of the first few months of data yielded no CH₄ detections and set a
16 new upper limit to 0.05 ppbv at 10 km slant altitude, lower than the background levels reported
17 by Curiosity at the surface. More generally, this upper limit strongly questioned all detections
18 reported before, unless a currently unknown rapid sink process is present, particularly in the
19 first few kilometers above the surface. In this paper, we present the first results from a dedicated
20 study of NOMAD data where methane, ethane and ethylene were targeted in solar occultation,
21 and we expand the search for these organics to more than half a Martian Year (MY). This
22 study's primary focus is the effort to detect a methane background level while attempts to
23 discover short-lived plume events were also undertaken.

24

25 **2. ExoMars TGO/NOMAD Instrument and Observation**

26 NOMAD consists of three high-resolution spectrometers; SO (Solar Occultation), LNO
27 (Limb, Nadir and Occultation) and UVIS (Ultraviolet and Visible Spectrometer). Technical
28 details on the two infrared channels (SO and LNO) are described in previous works (Vandaele
29 et al., 2018; Neefs et al., 2015; Thomas et al., 2016; Liuzzi et al., 2019; Crismani et al., 2020).
30 TGO's two-hour precessing nearly circular orbit allows for up to 24 occultations per Sol,
31 however the share assigned to NOMAD is typically 12-14 per Sol, with about one occultation
32 every orbit.

1 The SO channel operates in the wavelength range of 2.2 – 4.3 μm (2325-4350 cm^{-1}),
2 with a theoretical resolving power ($\lambda/\delta\lambda$) of 20,000 (Vandaele et al., 2018). The channel
3 combines an echelle grating spectrometer with an Acousto-Optical Tunable Filter (AOTF) to
4 select a wavelength region of interest. With a sampling rate of one second, SO provides a raw
5 vertical resolution of ~ 1 km spanning from near the surface (~ 5 km) to well above the exobase
6 (~ 200 km). As the AOTF is able to nearly instantaneously switch between diffraction orders,
7 the SO channel is capable of measuring up to six orders per second.

8 Solar occultations occur when the instrument is pointed at the solar disk while
9 observing the atmospheric absorption spectrum during ingress and egress. The spectra feature
10 high signal-to-noise ratios due to the strong solar source. The uppermost part (>200 km) of the
11 occultation corresponds to clear-Sun observations with no atmospheric absorption, which are
12 averaged to obtain a reference spectrum. To compute the transmittance for each measurement,
13 every spectrum below the top of atmosphere is then subsequently divided by the reference
14 spectrum (for details see Liuzzi et al., (2019) and Villanueva et al., (2020)).

15 As the instrument continuously samples closer to the surface and thereby intersects a
16 larger airmass, the atmospheric absorption increases which decreases the received signal. One
17 of the main limitations to trace gas detection is the presence of clouds and dust aerosols at
18 lower altitudes (Vandaele et al., 2018), which drastically reduces the intensity of light reaching
19 the instrument. Liuzzi et al., (2019) showed that the aerosol load in the Martian atmosphere
20 dramatically impacts the detectability of CH_4 and other trace species in SO geometry,
21 especially at occultation altitudes below 10 km. In SO, the primary sources of stochastic noise
22 in the instrument are the source noise, which depends on the intensity of the source signal
23 (Sun), and the digitization error (14 bits), which is significant when photon counts are low
24 (Neefs et al., 2015). Nevertheless, as long as the observed flux is above a certain threshold (a
25 few percent of the reference spectrum), noise will be dominated by the source, making SO the
26 most sensitive NOMAD channel for the detection of trace species, it also has the key capability
27 of enabling the characterization of their vertical distributions.

28 29 **3. Dataset and Trace Gas Retrievals**

30 The dataset presented here was acquired by NOMAD from April 2018 to April 2019,
31 corresponding to $L_s=162.5^\circ$ of MY 34 (Northern hemisphere late summer) to $L_s=15.0^\circ$ of MY
32 35 (northern hemisphere early spring). A total of 2,819 occultation events containing 243,172
33 individual spectra were analyzed. To target the molecules of interest (CH_4 , C_2H_6 , C_2H_4),

1 diffraction orders 133, 134 and 136 were used. Order 133 covers the wavenumber region 2988-
2 3012 cm^{-1} and includes C_2H_6 and C_2H_4 absorption features. Order 134 (3010-3035 cm^{-1})
3 contains the CH_4 ν_3 Q-branch which peaks at 3018 cm^{-1} , while order 136 (3055-3080 cm^{-1})
4 contains CH_4 R-branch lines ($J=3$ and higher). In absolute terms, the Q-branch is the most
5 intense CH_4 absorption feature, but it is not centered on the detector (diminishing signal at the
6 detector edges owing to reduced blaze throughput) and the presence of nearby solar lines
7 complicates the retrieval. The CH_4 lines in order 136 are more conveniently placed, the line at
8 3067 cm^{-1} (R4) appearing almost exactly at the center of the detector, however it is partially
9 overlapped by a water line, which occasionally degraded the quality of the retrieval (see spectra
10 in Figure 8).

11 The NOMAD detector has 256 rows, where the central 16 are fully illuminated by the
12 Sun. Rows are stacked in groups (i.e. bins) of four prior to any other data modification, and
13 this work utilizes a single such bin. Data calibration and instrument line shape characterization
14 is described in Liuzzi et al., (2019) and remains unmodified for this analysis. The present work
15 used NOMAD level 0.3a data, where the signal acquired by NOMAD is stored in terms of
16 detector counts. From these, data are pre-processed to derive transmittances, using as reference
17 the spectra acquired outside the atmosphere. The process is described in detail in previous
18 works (Aoki et al., 2019; Liuzzi et al., 2020). This pre-processing also takes into account any
19 instrumental temperature-induced frequency shift and produces frequency calibrated residuals.
20 Atmospheric retrievals (excluding CH_4 , C_2H_6 and C_2H_4) make use of the Planetary Spectrum
21 Generator (PSG, (Villanueva et al., 2018)), which employs a full atmospheric scattering and
22 radiative transfer package. PSG utilizes up-to-date molecular line lists and implements Optimal
23 Estimation techniques (Rodgers, 2000) modified with an extra regularization parameter
24 (Carissimo et al., 2005; Liuzzi et al., 2016) to perform retrievals, and was used successfully to
25 derive known atmospheric components such as H_2O , HDO and CO_2 (Vandaele et al., 2019;
26 Villanueva et al., 2020). The present work was performed by analyzing residual spectra that
27 were obtained once all known molecular lines along with stellar, water ice and broadband dust
28 features were fitted with PSG and filtered out, leaving only the eventual signal from minor
29 trace species in the residuals.

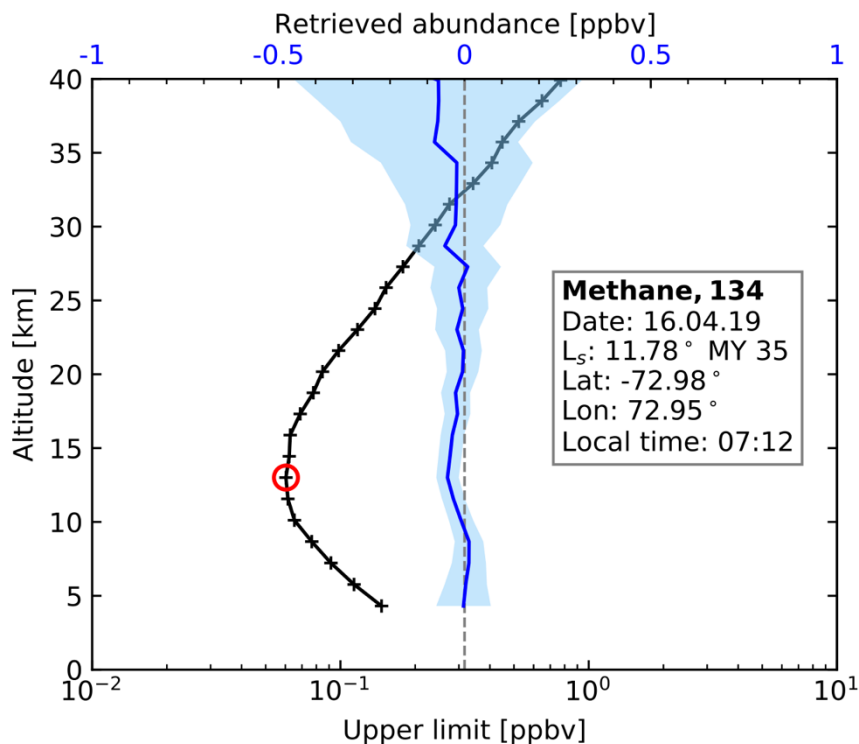
30 To limit the effects of the relevant noise sources in the SO channel, all measurements
31 whose continuum transmittance was below 5% were excluded from further analysis. Dust
32 storm season on Mars occurs every year from $L_s=180^\circ$ - 360° , when the planet is closest to the
33 Sun and overall surface and atmospheric temperatures are warmest (Smith, 2008). However,

1 MY 34 saw a higher dust aerosol load than normal as for the first time since 2007, Mars was
2 obscured by a Global Dust Storm (GDS). The GDS caused elevated dust aerosol loading across
3 the entire planet during $L_s=180^\circ$ - 250° , and from $L_s=315^\circ$ - 345° a strong regional dust storm
4 occurred (Smith, 2019). Due to the dust storm season on Mars, the most sensitive upper limits
5 were obtained using observations that were taken right after the beginning of science
6 operations, and also towards the end of this dataset.

7 In an effort to discover hydrocarbon signals, we compared measured atmospheric
8 residual spectra with synthetic trace gas spectra generated using PSG. The occurrence of
9 remnant broad continuum features in the residuals is still possible due to instrument variations
10 not fully accounted for (see Liuzzi et al., (2019) for further details). Therefore, after retrieval
11 of all expected species, a 3-spectrum moving mean was performed on the residuals to increase
12 sensitivity, with a resulting vertical resolution of typically 2 km. For diffraction order 136 (~
13 12% of the data), where the methane lines are sharp and narrow, a 10-pixel smoothed residual
14 spectrum was removed from the residual to mitigate some of the broader non-molecular
15 residual variability in the spectral continuum. This step is omitted for the other orders where
16 the absorption features are broader. A Levenberg-Marquardt least-squares method was used to
17 fit the atmospheric residuals to a synthetic spectrum produced with PSG, with prescribed
18 column abundances for the target species. The first and last ten pixels of each spectrum were
19 excluded from the fitting procedure due to diminishing signal at the detector edges owing to
20 reduced blaze throughput (see Liuzzi et al., (2019) for further discussion). The trace gas
21 retrieval used reduced chi-square analysis to determine retrieval parameters by minimization.

22 This algorithm produced two outputs for each retrieval: the covariance matrix of the
23 fitted parameters whose diagonal values correspond to the square of the uncertainty of every
24 parameter, and the optimal value for the scaling parameter, which corresponds to the relative
25 amplitude of the synthetic model that best fits the data. The upper limit is defined as the
26 retrieved uncertainty of the trace gas line-of-sight density divided by the total atmospheric line-
27 of-sight density. The attempted retrieved abundance is defined as the optimal scaling parameter
28 multiplied by the ratio of trace gas abundance in the synthetic model to CO_2 line-of-sight
29 density. A statistical sensitivity study was then carried out on these two values.

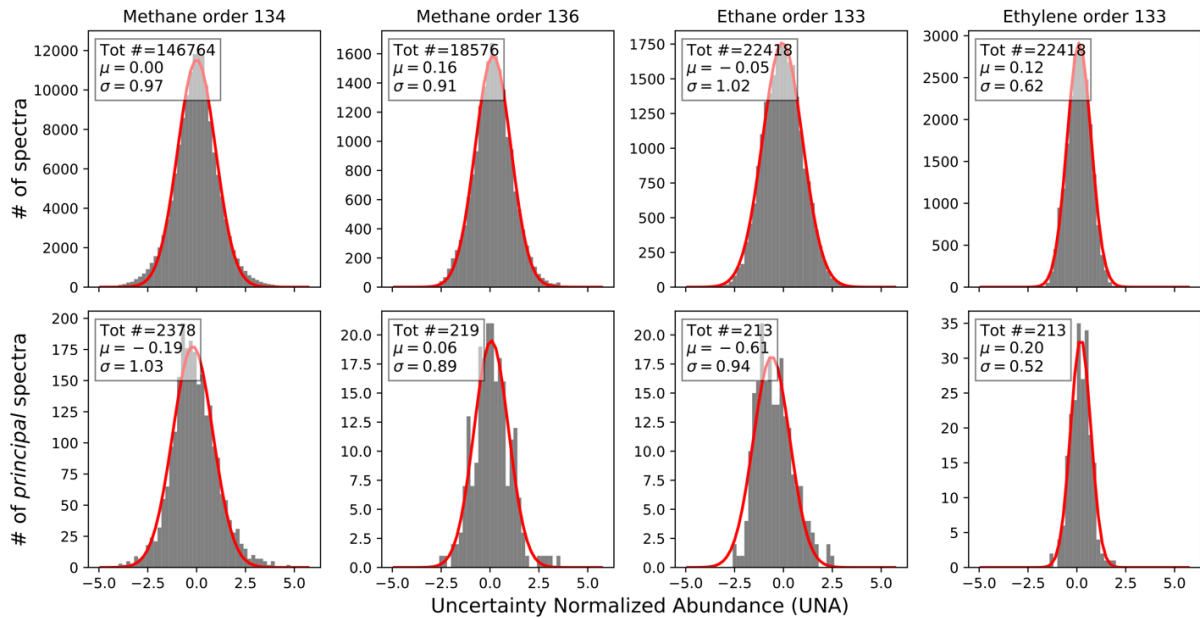
1 Figure 1 shows the retrieved abundance mixing ratio (blue) and 2- σ upper limit (black)
 2 (both in ppbv) by altitude for one occultation. At higher altitudes, the retrieved upper limits are
 3 dominated by the line-of-sight airmass, while at a certain point increasing aerosol opacity
 4 reduces the received signal such that low photon counts introduce noise from instrument
 5 systematics. The spectrum with the smallest upper limit is found where limiting factor is
 6 minimum, corresponding to a transition from one factor being dominant to the other. The
 7 altitude at which this transition occurs is dependent on the atmospheric aerosol opacity. The
 8 spectrum nearest this noise transition is henceforth referred to as the principal point.



9 **Figure 1:** An example of retrieved abundance (blue) and the corresponding derived upper
 10 limits (black) for all spectra in a single occultation as a function of altitude, targeting CH₄ in
 11 order 134. The shaded blue area indicates the $\pm 1-\sigma$ confidence interval. The red circle indicates
 12 the location of the principal point, the residual with smallest upper limit.

13
 14 To condense the dataset into a collection of the most relevant datapoints, a spectrum at
 15 or close in altitude to the principal point was selected for every occultation for each targeted
 16 trace gas. The retrieved abundances (in ppbv) for the selected spectra corresponding to these
 17 principal points were divided by their 1- σ uncertainty values, yielding the uncertainty
 18 normalized abundance (UNA). Assuming the estimated input noise in the retrieval is
 19 independent of geometric (latitude-longitude), seasonal (Ls), and orbital (e.g., heliocentric
 20 distance) factors, the histogram containing all UNA values should behave as a Gaussian

1 distribution with a standard deviation of one centered on the average UNA. If there is no
 2 detectable trace gas present and only random Gaussian noise is measured, given a large sample
 3 number, the histogram should be centered on zero. Figure 2 displays the histograms for each
 4 diffraction order, where the top row includes every spectrum from all occultations, and the
 5 bottom row includes only the principal point spectra, selected as demonstrated in Figure 1.



6 **Figure 2:** Histograms visualizing the distribution of retrieved abundances normalized by the
 7 $1\text{-}\sigma$ uncertainty value (UNA). The top row includes every data point from all occultations,
 8 while the bottom row includes only the principal point from each occultation. The two first
 9 columns show methane in orders 134 and 136, while the third and fourth columns show ethane
 10 and ethylene in order 133. The red curves show the Gaussian that best fits the dataset; the mean
 11 value (μ), standard deviation (σ) and total number of spectra are shown for each dataset.

12
 13 A standard deviation of less than one, as seen for the ethylene histograms, indicates that
 14 the true noise is larger than what was estimated for the retrieval. Order 134 was measured with
 15 significantly higher cadence than the other diffraction orders which aided in the statistical
 16 validity of the histogram results, where for Poisson-derived noise, the uncertainty on the
 17 sample mean is reduced with the square root of the sample size. In Section 4, only the principal
 18 point spectra from each occultation is evaluated. These measurements represent the most
 19 sensitive observations in the dataset and still number in the thousands for CH_4 and hundreds
 20 for C_2H_6 and C_2H_4 , an analysis of these observations are therefore statistically significant.

21
 22

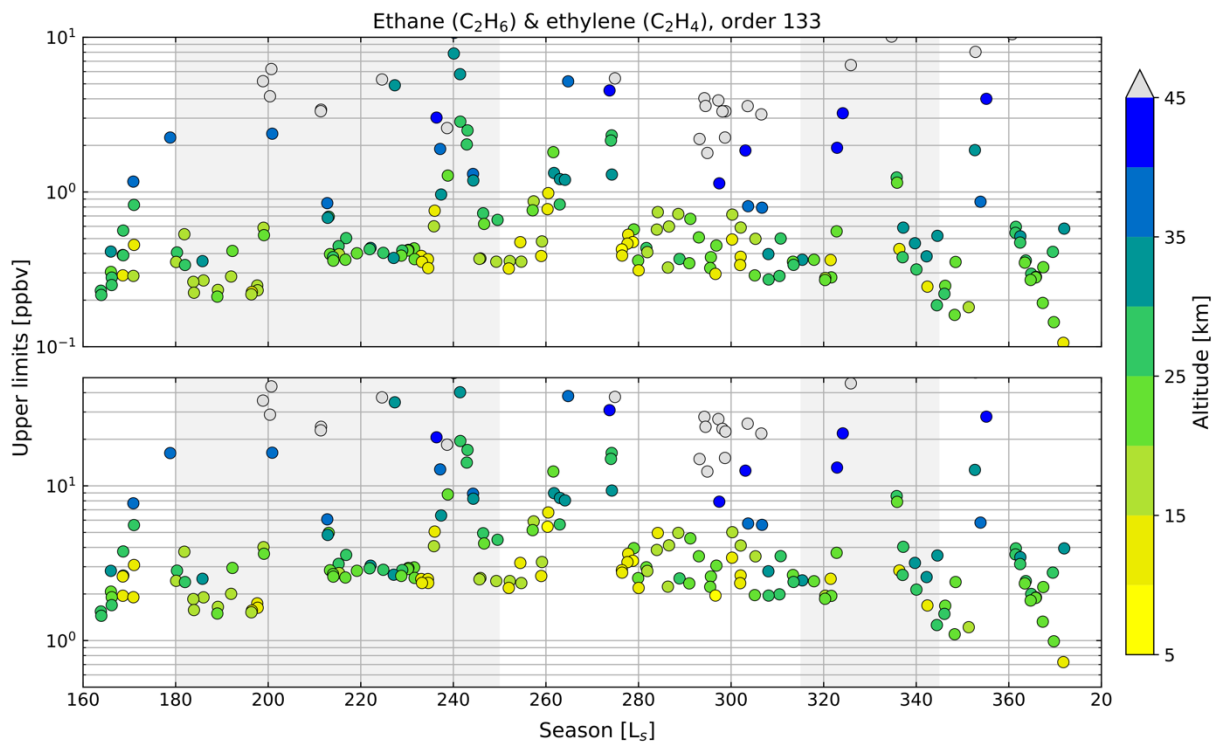
1 4. Results

2 This dataset samples the dawn and dusk terminators, latitudes from 85°S to 85°N, all
3 longitudes, and altitudes from 5-100 km. All altitude values used in this work are in terms of
4 true distance to the surface. Retrievals were organized by season and upper limit, where those
5 dedicated to CH₄ are subsequently arranged by longitude and latitude, as well as latitude and
6 altitude to explore various morphology aspects. The search for methane on Mars is twofold,
7 partly exploring the existence of a global, albeit low, seasonally varying background level
8 (Formisano et al., 2004; Geminale et al., 2008; Webster et al., 2018), and partly focusing on
9 the appearances of strong and localized short-term plumes (Giuranna et al., 2019; Mumma et
10 al., 2009; Webster et al., 2015). As the detection of short-lived events relies heavily on
11 observing the right place at the right time, this work prioritized the search for a CH₄ background
12 level.

13

14 4.1 Ethane & ethylene retrievals

15 Ethane and ethylene were targeted in 213 occultations (28,470 atmospheric spectra)
16 using order 133. The principal point (spectrum with the smallest retrieved upper limit in each
17 occultation) was selected by the approach described in Section 3 and visualized in Figure 1.
18 C₂H₆ and C₂H₄ upper limits are plotted in Figure 3 where they are shown as a function of
19 season, the color scale indicates altitude.



1 **Figure 3:** The principal point (smallest upper limit) for each occultation below 10 ppbv, for
2 ethane (top panel) and ethylene (bottom panel) in order 133, shown as a function of season,
3 where the colors indicate altitude. Shaded gray areas indicate times of enhanced aerosol
4 opacity.

5

6 The retrieved upper limits demonstrably degraded as dust storm season and the GDS
7 commenced at $L_s=180^\circ$ with higher dust aerosol opacity reducing the received signal along the
8 line of sight. Even as the GDS dissipated around $L_s=250^\circ$, the upper limits remained high until
9 some time after the dust storm season ended at $L_s=360^\circ$. The enhanced aerosol content in the
10 lower atmosphere raised the altitude of the principal points, resulting in the smallest upper
11 limits for ethane and ethylene being obtained around $L_s=12^\circ$.

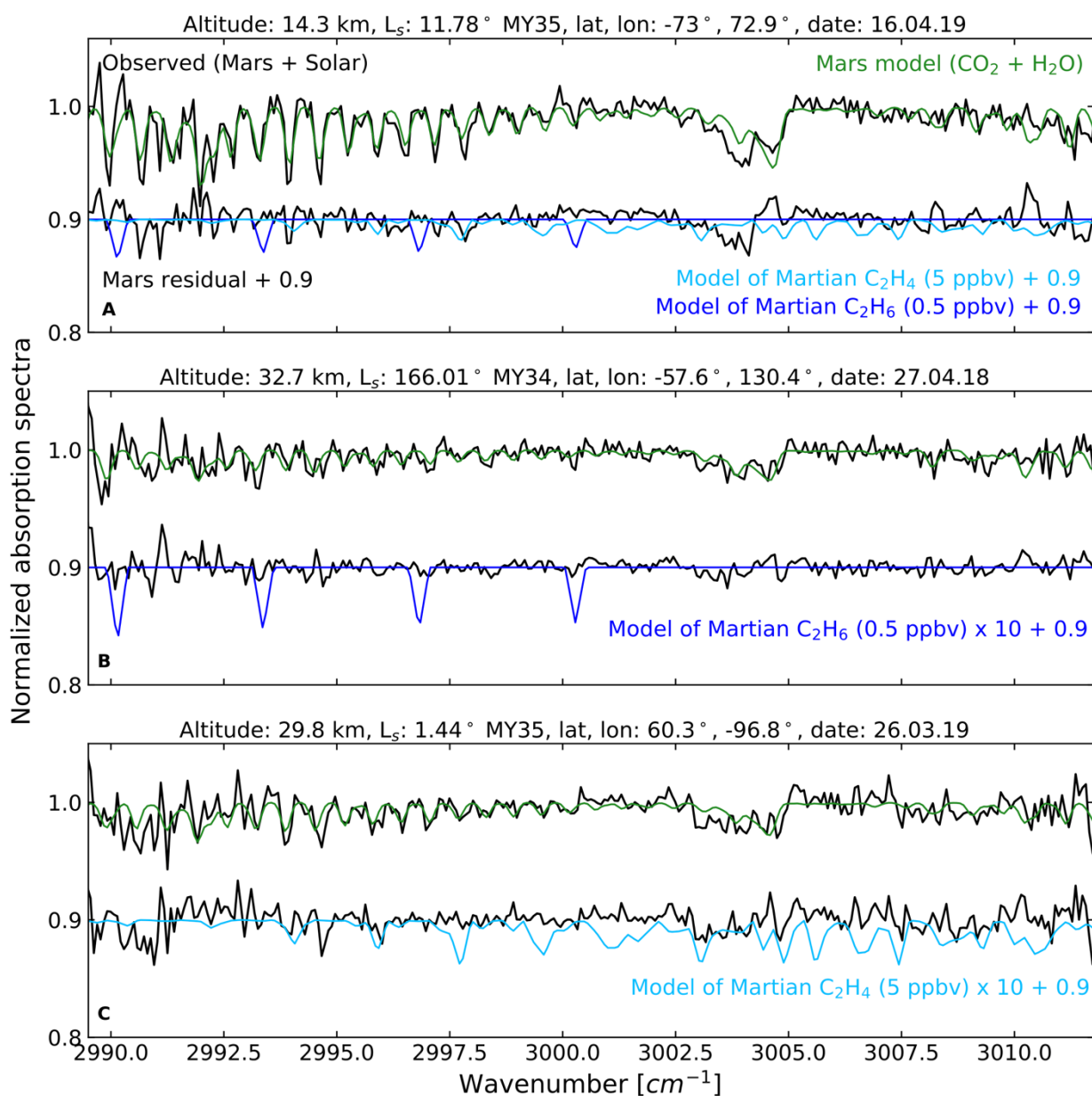
12

13 The smallest upper limits are useful when searching for a low, global background level
14 of a trace gas, and such a spectrum is shown in Figure 4, panel A. As ethane and ethylene have
15 relatively short photochemical lifetimes in the Martian atmosphere, a constantly present
16 background level requires continuous replenishment. Therefore, in the attempt to discover
17 short-lived plumes, the most suitable strategy is to investigate spectra with high UNA, falling
18 on the right wing of the histograms in Figure 2. Residuals for the measurement with highest
19 UNA below 30 km for each gas are shown in Figure 4B and 4C. Known solar and Martian
20 atmospheric absorption lines were removed, leaving featureless residual spectra. The lowest
21 upper limit for ethane was determined to be 0.11 ppbv, and 0.7 ppbv for ethylene, both
22 significantly lower than previous upper limits (see Table 1). The upper limits obtained for the
23 high UNA spectra are 0.4 ppbv (UNA =2.23) and 3.6 ppbv (UNA =1.25) for ethane and
24 ethylene respectively. The high UNA is the result of a combination of relatively high retrieved
25 abundance and a comparably low noise level.

26

27

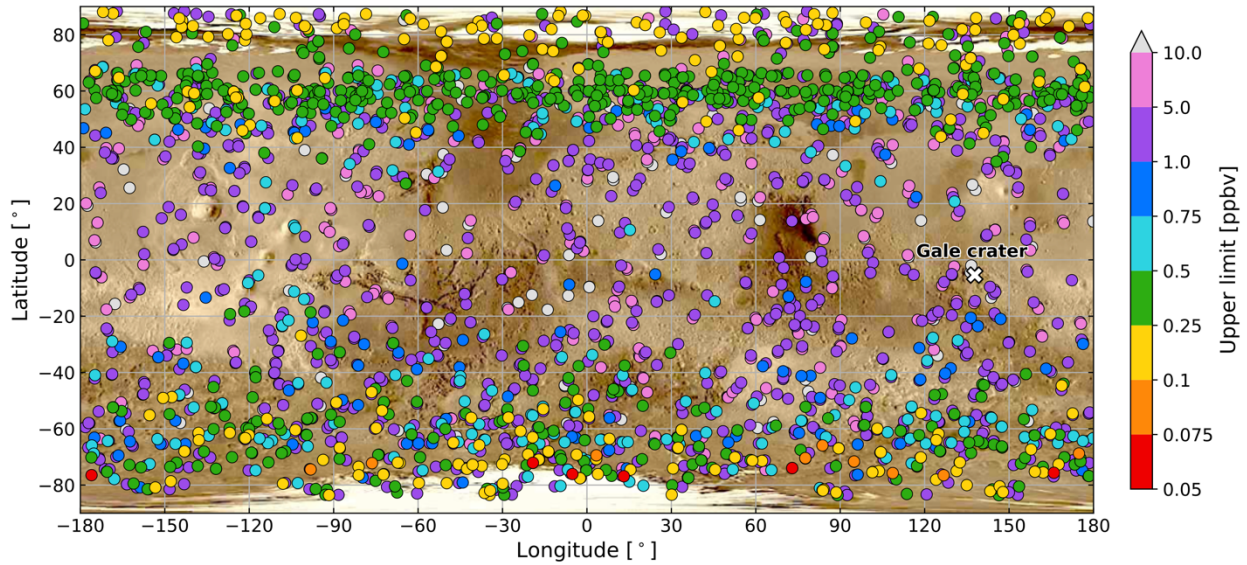
28



1 **Figure 4:** Sensitive search for ethane and ethylene on Mars. A) targeting spectra with smallest
 2 upper limits. B) & C) targeting spectra with high UNA. Observed spectra in black, PSG model
 3 fit to the Martian atmosphere in green, synthetic spectra of trace species in hues of blue.

4.2 Methane retrievals

6 The search for CH₄ is one of the primary objectives of ExoMars TGO and NOMAD
 7 (Vandaele et al., 2015). For this work, order 134 is used to target the CH₄ Q-branch, while
 8 order 136 contains the R-branch lines. The dataset includes 2,385 occultations where order 134
 9 was measured, along with 221 occultations for order 136, totaling more than 210,000 spectra
 10 able to target methane. For each occultation, a spectrum near in altitude to the principal point
 11 was selected and the upper limits are mapped onto the Martian surface in Figure 5.



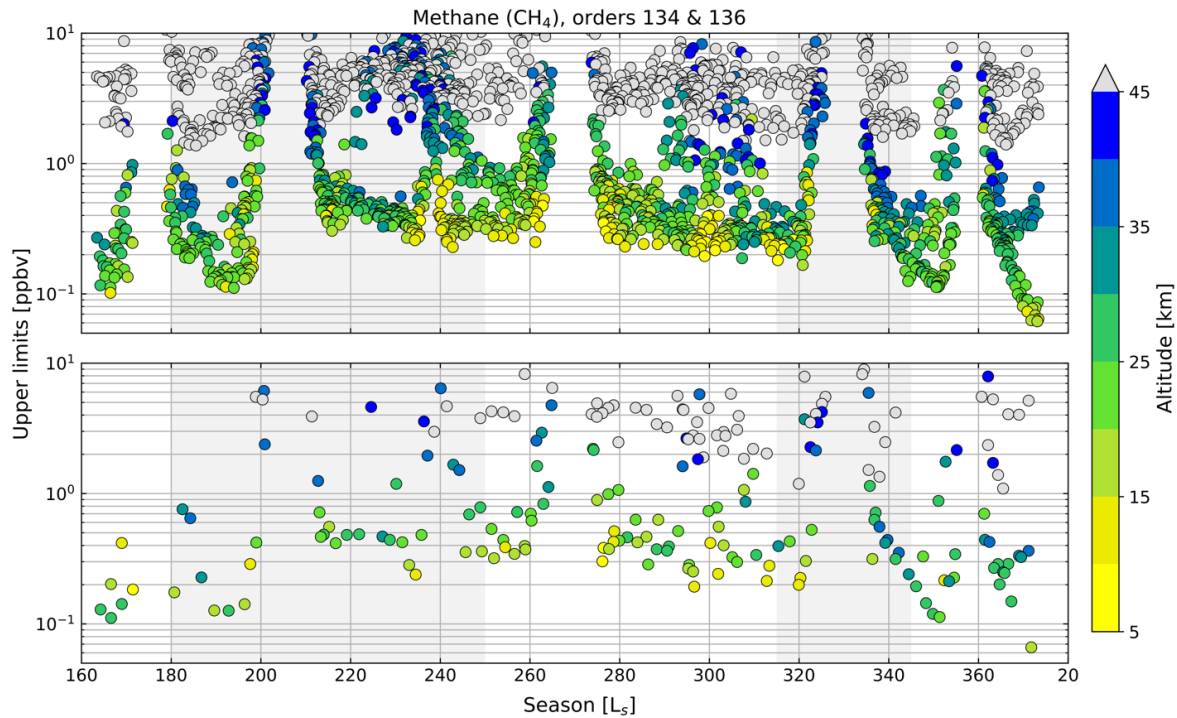
1 **Figure 5:** All principal points for CH₄ in orders 134 and 136. Visualized on a latitude-longitude
 2 map with Gale crater (position of Curiosity rover) marked by a white cross. Colors indicate the
 3 derived upper limits for abundance values within a 95% confidence interval ($2\text{-}\sigma$). The
 4 indicators are sorted, with the smallest upper limits shown on top.

5

6 Methane measurements span all longitudes and latitudes, however datapoints at low
 7 latitudes have larger upper limits than those found at higher latitudes. This correlation is
 8 attributed to the tendency of lower latitudes typically having a higher dust aerosol load than
 9 high-latitude regions, which raised the atmospheric opacity near equatorial latitudes and thus
 10 prevented sensitive measurements. The low number of measurements near the equator ($\pm 20^\circ$)
 11 is related to the orbital geometry of solar occultation measurements, representing 10% of the
 12 total number of measurements. Low latitude datapoints subsequent to April 2019 are expected
 13 to have higher sensitivity as Mars enters the aphelion season, during which dust activity is
 14 greatly reduced (Smith, 2008).

15

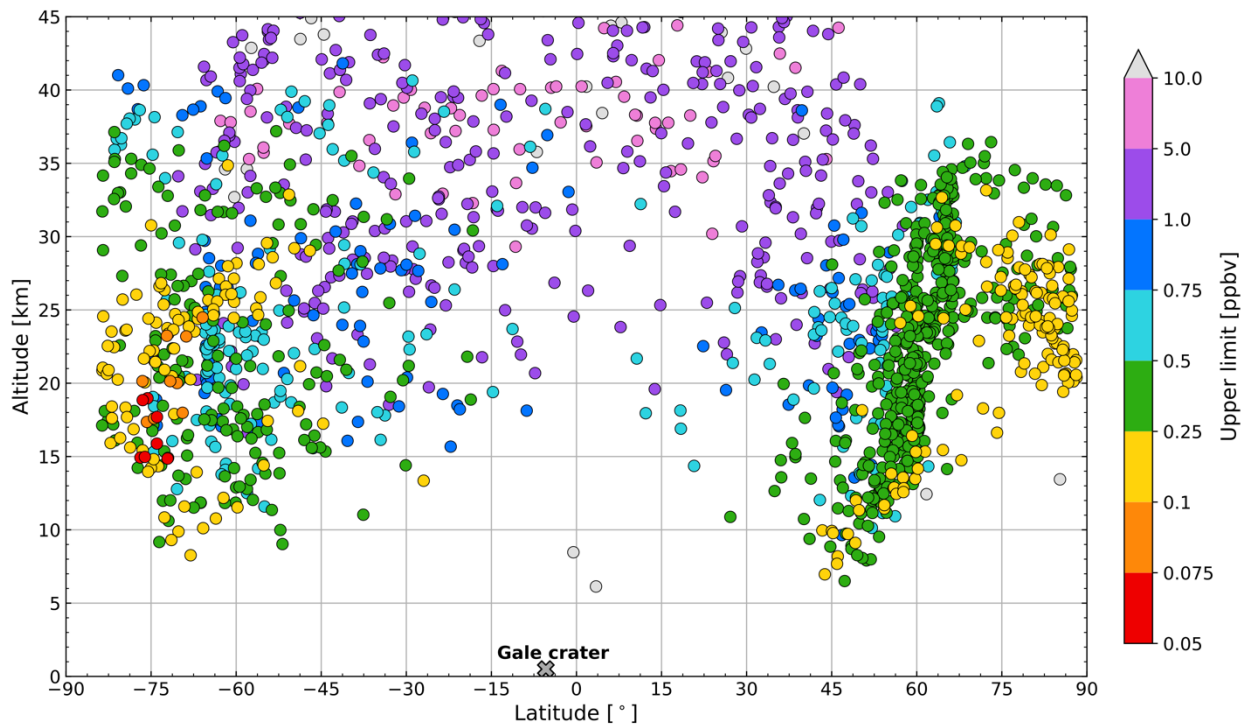
16 Due to the orbit of TGO, latitudinal changes are convolved with seasonal variation,
 17 since the orbit precesses on a timescale similar to expected seasonal changes. The best upper
 18 limit for each occultation is presented in Figure 6 as a function of Martian season L_s . The
 19 principal points with the lowest upper limits were obtained at the beginning and towards the
 20 end of TGO's first year of observations. They tend to be taken at lower altitudes where the
 spacecraft is observing through a large airmass, which increases the relative depth of the lines.



1 **Figure 6:** The principal points for CH₄ from each occultation, for order 134 (top row) and 136
 2 (bottom row) plotted as a function of season, where the colors indicate altitude. Methane upper
 3 limits increased significantly while the planet was engulfed by the GDS (L_s=195°-280°).
 4 Shaded gray areas indicate times of enhanced aerosol opacity.

5
 6 Methane upper limits have been explored spatially in Figure 5, and as a function of
 7 time (season) in Figure 6. In order to explore the altitude distribution of the upper limits,
 8 Figure 7 shows the principal points for CH₄ for all longitudes from all occultations as a
 9 function of latitude and altitude. Figure 7 demonstrates that even in the presence of two dust
 10 storms, a large number of sensitive measurements probed altitudes below the lowest two
 11 scale heights (<20 km). Grain-gas interactions in the lower one to two scale heights such as
 12 oxidization (Atreya et al., 2006) and reactions with eroded quartz (Knak Jensen et al., 2014)
 13 have been proposed as potential, and the latter is currently considered one of the most
 14 plausible candidates for a CH₄ loss process (Yung et al., 2018). However, as NOMAD is
 15 obtaining high-sensitivity measurements down into the lowest scale height of the Martian
 16 atmosphere, this hypothesis may require additional investigation to be considered feasible in
 17 the Martian atmosphere.

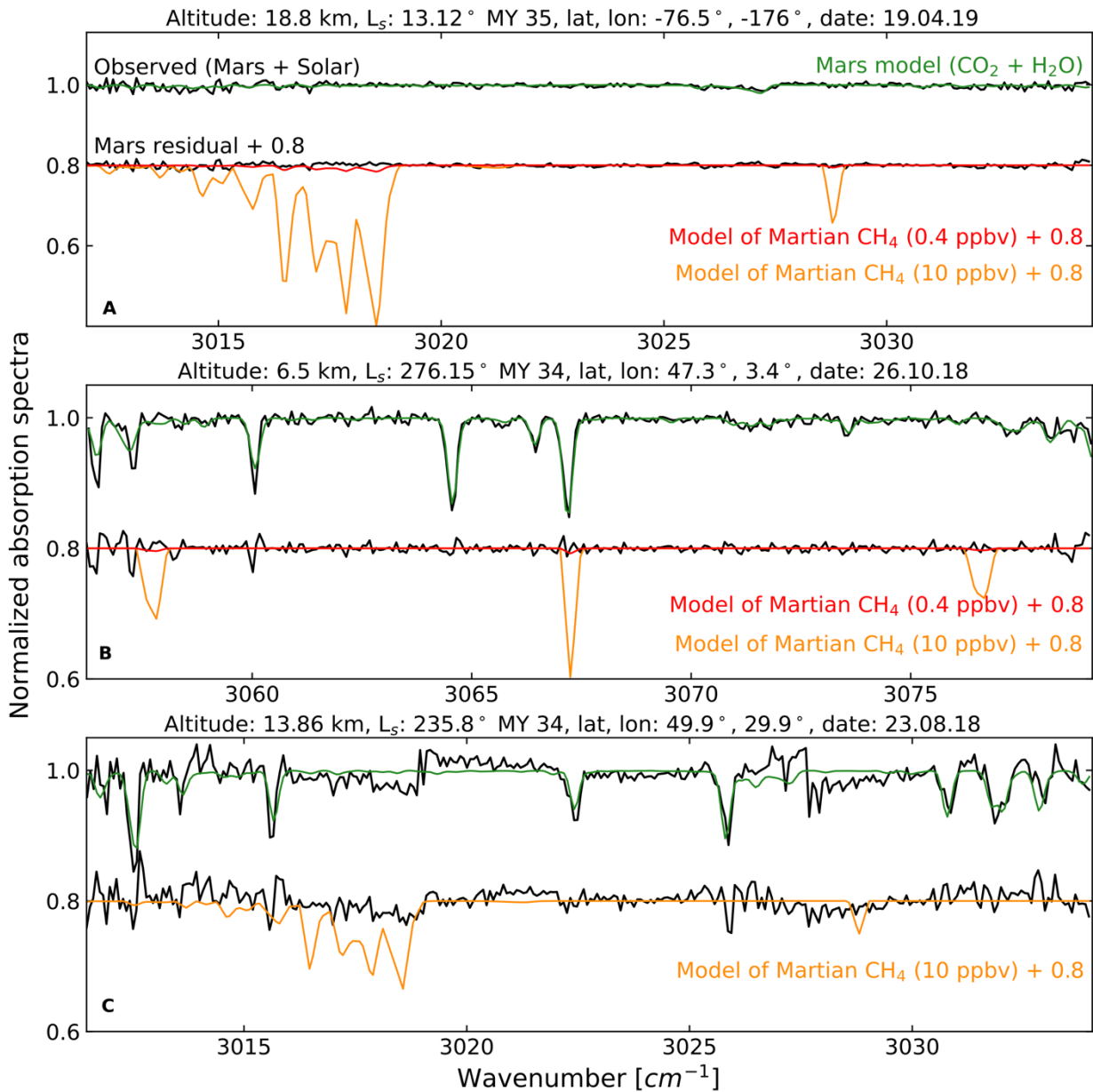
18



1 **Figure 7:** Principal CH₄ points from all occultations for diffraction orders 134 and 136 for all
 2 longitudes, as a function of altitude and latitude. The colors indicate upper limits. Green,
 3 yellow, orange and red indicators are values at or below the average background level
 4 observed by Webster et al., (2018). The gray cross indicates position of the Curiosity rover in
 5 Gale crater.

6

7 To establish whether a persistent background level of methane can be detected by
 8 NOMAD, the principal points would need to be collected and analyzed as a whole, whereas
 9 selecting the measurements with the highest UNA is a more appropriate approach when
 10 searching for short-lived events such as potential plumes. The entire principal point dataset
 11 contains five measurements with UNA at or above 5- σ . To investigate such a high σ
 12 “detection”, Figure 8C is constructed to highlight the residual of a principal point spectrum
 13 located at the positive wing of the histograms in Figure 2. The spectrum in Figure 8C has an
 14 UNA of 5.1, suggesting a 5- σ detection of 0.66 ppbv. However, upon inspection of the
 15 residual it becomes evident that there is no clear detection of CH₄, and instead this 5- σ result
 16 is the consequence of residual systematics related to digitization error. Generally, the
 17 occurrence of high- σ detections is an expected effect when measuring Poisson noise on
 18 repeated observations. Table 2 presents a summary of the upper limits and the geophysical
 19 details for each spectrum shown in Figure 8.



1 **Figure 8:** Search for methane on Mars by three methods; A) spectrum with lowest retrieved
 2 upper limit, B) spectrum with principal point closest to surface, C) spectrum with high UNA
 3 in search of plume. Observed spectra are shown in black, PSG model fit to the main gases
 4 (H₂O and CO₂) in green and synthetic CH₄ spectra in red and orange. The red spectrum of 0.4
 5 ppbv abundance is used to visualize previously observed background level and the orange
 6 spectrum of 10 ppbv abundance simulates a sporadic plume event.

7

8 The spectrum with lowest upper limit obtained from this entire study is shown in
 9 Figure 8A, with a retrieved upper limit of 0.061 ppbv. The spectrum closest to the surface
 10 (Figure 8B) has a retrieved upper limit of 0.30 ppbv, and the spectrum with an UNA of 5
 11 (Figure 8C) has an upper limit of 0.66 ppbv. The most sensitive measurement and the one

1 with highest UNA were achieved with order 134, while the spectrum lowest in altitude was
2 attained with order 136. The residual spectra displayed in Figure 8 are without significant
3 features and considering the strong signal a plume-like event is likely to cause, NOMAD
4 would be able to detect it if present in the current data set or in the future.
5

6 **5. Discussion**

7 Methane detections reported by several groups over the past fifteen years suggest
8 localized regions of sporadic gaseous release from unknown sources and with an unknown
9 fast and efficient destruction mechanism. Previous ground-based and Mars Express orbital
10 detections reported column densities for the whole atmosphere, apart from Curiosity which
11 takes measurements at the surface within Gale crater. The data presented here are solar
12 occultation measurements, sampling the atmosphere at specific slant heights, obtaining a
13 typical vertical resolution of 2 km, with the lowest measured principal point close to 6 km
14 above the Martian surface. CH₄ background levels have been reported to vary, perhaps on a
15 seasonal basis, and a large outgassing event was reportedly detected by two independent
16 teams (Giuranna et al., 2019; Webster et al., 2015). From our current understanding of the
17 Martian atmosphere, any seasonal, periodic or even sporadic release of CH₄ will lead to its
18 accumulation over time, increasing the chances for its detection (Lefèvre, 2019). Moreover,
19 any methane released from the surface would in the matter of days be transported to altitudes
20 where it could be detected by TGO/NOMAD (Viscardy et al., 2016). Geminale et al., (2011)
21 reported a strong increase in CH₄ up to 45 ppbv over the northern polar cap during northern
22 summer, along with higher abundances in general during northern spring compared to fall
23 and winter, related to a possible methane source under the polar cap. However, Lefèvre and
24 Forget (2009) showed that in the event of a methane release, the gas would quickly be
25 globally distributed, and during northern winter a large enrichment in methane mixing ratio
26 resulting from the condensation of CO₂ gas at high latitudes would occur. TGO/NOMAD
27 sampled high latitudes during late northern summer as well as northern winter and found no
28 detections during either season.

29 All reported CH₄ detections, apart from the Curiosity measurements and the Giuranna
30 et al., (2019) findings from June 2013, are at least eleven years old. The most recently
31 reported background level from MSL/TLS claimed 0.319 ppbv on May 17th, 2017 (Webster
32 et al., 2018), less than an Earth year prior to TGO's first measurements which revealed an
33 upper limit three times lower. The largest plume ever recorded, and the most recent MSL

1 methane data, was mentioned in Moores et al., (2019b), with a value of 19 ± 3 ppbv on June
2 20th 2019, while NOMAD data acquired only two months earlier yielded some of the lowest
3 upper limits obtained with the instrument. It is important to note that Curiosity/MSL samples
4 the atmosphere at the surface, while no TGO/NOMAD measurements below 6 km have been
5 analyzed in this work. To reconcile these results, one would need to include an atmospheric
6 process where CH₄ is rapidly removed from the lower atmosphere. Any such strong
7 destruction mechanism should not affect known and confirmed knowledge about the Martian
8 atmosphere and its chemical composition.

9 Moores et al., (2019a) explored the possibility of a diurnal cycle to reconcile MSL
10 and TGO observations by modeling a surface microseepage flux and diffusivity in the
11 Martian nighttime atmosphere. They propose an inhibition of atmospheric mixing near the
12 Gale crater surface overnight, enabling methane being emitted to accumulate. Another
13 reconciling process could be by direct electron dissociation during dust storms (Farrell et
14 al., 2006), but highly sensitive NOMAD measurements right before the dust storm, when
15 there could have been methane present, show extremely low upper limits (Figure 6). Other
16 grain-gas interactions could take place near the surface; oxidant-covered soil particles could
17 rapidly oxidize CH₄ before it can be transported to other regions (Atreya et al., 2006), or
18 methane could be sequestered by eroded quartz grains (Knak Jensen et al., 2014). The latter
19 mechanism is considered quite plausible (Yung et al., 2018), although its efficiency has been
20 questioned (Lefèvre, 2019) and the laboratory work did not include any other atmospheric
21 species in their experiment apart from CO₂, thus neglecting the impact on and by other
22 species (Knak Jensen et al., 2014). It should be noted that NOMAD's most sensitive searches
23 are between 6-15 km in altitude (Figure 7).

24 Localized surface sinks have been explored by Lefèvre and Forget (2009), who found
25 that for their model to match observations, methane would have a lifetime of an hour at the
26 atmosphere-regolith interface. Any additional mechanism dominating the removal of CH₄, has
27 to be more efficient than currently understood photochemistry by a factor of ≥ 100 and would
28 need to destroy or sequester CH₄ without violating the chemistry of active species such as O₃,
29 CO or H₂O₂, which are reproduced by existing models without unknown processes. If methane
30 is indeed released from sub-surface reservoirs into the Martian atmosphere, the question of a
31 strong destruction mechanism remains unresolved. To reconcile results from MSL and TGO,
32 future work would benefit from focusing on understanding near-surface destruction
33 mechanisms.

34

6. Conclusion

In this study, methane, ethane and ethylene retrieval attempts were conducted on atmospheric residual spectra (see Table 2). In contrast with previous total atmospheric column measurements (i.e., ground-based, Mars-Express) and surface measurements (i.e., MSL), TGO is able to probe the atmosphere with high sensitivities above 6 km and with fine vertical resolution (~2 km as presented here). The uncertainty normalized abundances follow a Gaussian distribution and their mean values are at or close to zero, suggesting there are no detections of organics in the dataset, thus the upper limit is defined as the $2\text{-}\sigma$ uncertainty value for each retrieval. The upper limits presented in this work, and the detection limit of NOMAD, are at this moment dominated by systematics. Future efforts should focus on improvements in NOMAD characterization stability across the occultation, and refining the modeling of known molecular lines with an improved instrument lineshape. Furthermore, expansion of the dataset beyond the Martian dust season will yield more sensitive datapoints at low latitudes and altitudes.

The upper limits for ethane and ethylene provide significant improvements compared to previous studies, lowering these by a factor of 2-5. However, the values are at least a factor of six higher than the methane upper limit, and thus cannot contribute to narrowing down possible origins for the hydrocarbons, if they were found to be present.

Methane detection attempts were made at all latitudes and longitudes, at slant altitudes from 5-100 km, and sampled at dawn and dusk local times. No background level of CH_4 was detected down to 0.06 ppbv, and no intense short-lived plume events were observed. Our methane upper limit is consistent with the average value reported by Korablev et al., (2019). If methane is being released into the atmosphere, this process would need to be sporadic and undetected in this year of observations. Moreover, whether the presumed release is global or local, an unknown destruction mechanism would also need to be efficiently remove the methane before vertical mixing can bring it above 6 km (i.e. within a few days (Viscardy et al., 2016)), or else the release is local and concentrated enough that mixing depletes the concentrations well below any potential detection threshold at those altitudes accessible by TGO/NOMAD.

Trace gas	Upper limit	Altitude	Lat, Lon	Ls	Date
Methane	0.061 ppbv	18.8 km	-76.5°, -176°	13.12°	19.04.19
Ethane	0.1 ppbv	14.3 km	-73°, 72.9°	11.78°	16.04.19
Ethylene	0.7 ppbv	14.3 km	-73°, 72.9°	11.78°	16.04.19

Table 2: The lowest obtained upper limits for the three target species. Lowest methane upper limits achieved with order 134. Ethane and ethylene were both retrieved from order 133.

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References

- Allen, M., Sherwood Lollar, B., Runnegar, B., Oehler, D.Z., Lyons, J.R., et al., 2006. Is Mars alive? *Eos Trans. Am. Geophys. Union* 87, 433.
<https://doi.org/10.1029/2006EO410001>
- Aoki, S., Richter, M.J., DeWitt, C., Boogert, A., Encrenaz, T., et al., 2018. Stringent upper limit of CH₄ on Mars based on SOFIA/EXES observations. *Astron. Astrophys.* 610, A78. <https://doi.org/10.1051/0004-6361/201730903>
- Aoki, S., Vandaele, A.C., Daerden, F., Villanueva, G.L., Liuzzi, G., et al., 2019. Water Vapor Vertical Profiles on Mars in Dust Storms Observed by TGO/NOMAD. *J. Geophys. Res. Planets* 124, 3482–3497. <https://doi.org/10.1029/2019JE006109>
- Atreya, S.K., Gu, Z.G., 1995. Photochemistry and stability of the atmosphere of Mars. *Adv. Space Res.* 16, 57–68. [https://doi.org/10.1016/0273-1177\(95\)00250-1](https://doi.org/10.1016/0273-1177(95)00250-1)
- Atreya, S.K., Wong, A.-S., Renno, N.O., Farrell, W.M., Delory, G.T., et al., 2006. Oxidant Enhancement in Martian Dust Devils and Storms: Implications for Life and Habitability. *Astrobiology* 6, 439–450. <https://doi.org/10.1089/ast.2006.6.439>
- Bernard, B., Brooks, J.M., Sackett, W.M., 1977. A Geochemical Model For Characterization Of Hydrocarbon Gas Sources In Marine Sediments, in: Offshore Technology Conference. Presented at the Offshore Technology Conference, Offshore Technology Conference, Houston, Texas. <https://doi.org/10.4043/2934-MS>
- Carissimo, A., De Feis, I., Serio, C., 2005. The physical retrieval methodology for IASI: the δ -IASI code. *Environ. Model. Softw.* 20, 1111–1126.
<https://doi.org/10.1016/j.envsoft.2004.07.003>
- Carr, M.H., 1996. Water erosion on Mars and its biologic implications. *Endeavour* 20, 56–60.
[https://doi.org/10.1016/0160-9327\(96\)10013-2](https://doi.org/10.1016/0160-9327(96)10013-2)
- Chastain, B.K., Chevrier, V., 2007. Methane clathrate hydrates as a potential source for martian atmospheric methane. *Planet. Space Sci.* 55, 1246–1256.
<https://doi.org/10.1016/j.pss.2007.02.003>
- Conrad, R., 2009. The global methane cycle: recent advances in understanding the microbial processes involved: Global methane cycle. *Environ. Microbiol. Rep.* 1, 285–292.
<https://doi.org/10.1111/j.1758-2229.2009.00038.x>
- Crismani, M.M.J., Schneider, N.M., Plane, J.M.C., 2017a. Comment on “A cometary origin for atmospheric martian methane” by Fries et al., 2016. *Geochem. Perspect. Lett.*
<https://doi.org/10.7185/geochemlet.1715>
- Crismani, M.M.J., Schneider, N.M., Plane, J.M.C., Evans, J.S., Jain, S.K., et al., 2017b. Detection of a persistent meteoric metal layer in the Martian atmosphere. *Nat. Geosci.* 10, 401–404. <https://doi.org/10.1038/ngeo2958>
- Crismani, M.M.J., Villanueva, G.L., Liuzzi, G., Smith, M.D., Knutsen, E.W., et al., 2020. A Global and Seasonal Perspective of Martian Water Vapor from ExoMars/NOMAD.
- Encrenaz, T., 2008. Search for methane on Mars: Observations, interpretation and future work. *Adv. Space Res.* 42, 1–5. <https://doi.org/10.1016/j.asr.2007.01.069>
- Etioppe, G., Ehlmann, B.L., Schoell, M., 2013. Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars. *Icarus* 224, 276–285.
<https://doi.org/10.1016/j.icarus.2012.05.009>
- Farrell, W.M., Delory, G.T., Atreya, S.K., 2006. Martian dust storms as a possible sink of atmospheric methane. *Geophys. Res. Lett.* 33, L21203.
<https://doi.org/10.1029/2006GL027210>
- Flynn, G.J., 1996. The Delivery of Organic Matter from Asteroids and Comets to the Early Surface of Mars, in: Rickman, H., Valtonen, M.J. (Eds.), *Worlds in Interaction: Small Bodies and Planets of the Solar System*. Springer Netherlands, Dordrecht, pp. 469–

- 1 474. https://doi.org/10.1007/978-94-009-0209-1_58
- 2 Fonti, S., Mancarella, F., Liuzzi, G., Roush, T.L., Chizek Frouard, M., et al., 2015. Revisiting
3 the identification of methane on Mars using TES data. *Astron. Astrophys.* 581, A136.
4 <https://doi.org/10.1051/0004-6361/201526235>
- 5 Fonti, S., Marzo, G.A., 2010. Mapping the methane on Mars. *Astron. Astrophys.* 512, A51.
6 <https://doi.org/10.1051/0004-6361/200913178>
- 7 Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N., Giuranna, M., 2004. Detection of
8 Methane in the Atmosphere of Mars. *Science* 306, 1758–1761.
9 <https://doi.org/10.1126/science.1101732>
- 10 Fries, M., Christou, A., Archer, D., Conrad, P., Cooke, W., et al., 2016. A cometary origin for
11 martian atmospheric methane. *Geochem. Perspect. Lett.* 2, 10–23.
12 <https://doi.org/10.7185/geochemlet.1602>
- 13 Geminale, A., Formisano, V., Giuranna, M., 2008. Methane in Martian atmosphere: Average
14 spatial, diurnal, and seasonal behaviour. *Planet. Space Sci.* 56, 1194–1203.
15 <https://doi.org/10.1016/j.pss.2008.03.004>
- 16 Geminale, A., Formisano, V., Sindoni, G., 2011. Mapping methane in Martian atmosphere
17 with PFS-MEX data. *Planet. Space Sci.* 59, 137–148.
18 <https://doi.org/10.1016/j.pss.2010.07.011>
- 19 Gillen, E., Rimmer, P.B., Catling, D.C., 2020. Statistical analysis of Curiosity data shows no
20 evidence for a strong seasonal cycle of martian methane. *Icarus* 336, 113407.
21 <https://doi.org/10.1016/j.icarus.2019.113407>
- 22 Giuranna, M., Viscardy, S., Daerden, F., Neary, L., Etiope, G., et al., 2019. Independent
23 confirmation of a methane spike on Mars and a source region east of Gale Crater. *Nat.*
24 *Geosci.* 12, 326–332. <https://doi.org/10.1038/s41561-019-0331-9>
- 25 Grebowsky, J.M., Benna, M., Plane, J.M.C., Collinson, G.A., Mahaffy, P.R., et al., 2017.
26 Unique, non-Earthlike, meteoritic ion behavior in upper atmosphere of Mars: Mars
27 Metal Ions. *Geophys. Res. Lett.* 44, 3066–3072.
28 <https://doi.org/10.1002/2017GL072635>
- 29 Grotzinger, J.P., Sumner, D.Y., Kah, L.C., Stack, K., Gupta, S., et al., 2014. A Habitable
30 Fluvio-Lacustrine Environment at Yellowknife Bay, Gale Crater, Mars. *Science* 343,
31 1242777–1242777. <https://doi.org/10.1126/science.1242777>
- 32 Haberle, R.M., Clancy, R.T., Forget, F., Smith, M.D., Zurek, R.W., et al., 2017. *The*
33 *Atmosphere and Climate of Mars*. Cambridge University Press.
- 34 Holmes, J.A., Patel, M.R., Lewis, S.R., 2017. The vertical transport of methane from
35 different potential emission types on Mars: VERTICAL TRANSPORT OF
36 METHANE ON MARS. *Geophys. Res. Lett.* 44, 8611–8620.
37 <https://doi.org/10.1002/2017GL074613>
- 38 Knak Jensen, S.J., Skibsted, J., Jakobsen, H.J., ten Kate, I.L., Gunnlaugsson, H.P., et al.,
39 2014. A sink for methane on Mars? The answer is blowing in the wind. *Icarus* 236,
40 24–27. <https://doi.org/10.1016/j.icarus.2014.03.036>
- 41 Korablev, O., Montmessin, F., Fedorova, A.A., Trokhimovskiy, A., Forget, F., et al., 2019.
42 No detection of methane on Mars from early ExoMars Trace Gas Orbiter
43 observations. *Nature* 568, 517–520. <https://doi.org/10.1038/s41586-019-1096-4>
- 44 Krasnopolsky, V.A., 2012. Search for methane and upper limits to ethane and SO₂ on Mars.
45 *Icarus* 217, 144–152. <https://doi.org/10.1016/j.icarus.2011.10.019>
- 46 Krasnopolsky, V.A., 2007. Long-term spectroscopic observations of Mars using
47 IRTF/CSHELL: Mapping of O₂ dayglow, CO, and search for CH₄. *Icarus* 190, 93–
48 102. <https://doi.org/10.1016/j.icarus.2007.02.014>
- 49 Krasnopolsky, V.A., 2006. Some problems related to the origin of methane on Mars. *Icarus*
50 180, 359–367. <https://doi.org/10.1016/j.icarus.2005.10.015>

- 1 Krasnopolsky, V.A., Bjoraker, G.L., Mumma, M.J., Jennings, D.E., 1997. High-resolution
2 spectroscopy of Mars at 3.7 and 8 μm : A sensitive search for H_2O , CO , HCl ,
3 and CH_4 , and detection of HDO. *J. Geophys. Res. Planets* 102, 6525–6534.
4 <https://doi.org/10.1029/96JE03766>
- 5 Krasnopolsky, V.A., Maillard, J.P., Owen, T.C., 2004. Detection of methane in the martian
6 atmosphere: evidence for life? *Icarus* 172, 537–547.
7 <https://doi.org/10.1016/j.icarus.2004.07.004>
- 8 Lefèvre, F., 2019. The Enigma of Methane on Mars, in: Cavalazzi, B., Westall, F. (Eds.),
9 Biosignatures for Astrobiology, Advances in Astrobiology and Biogeophysics.
10 Springer International Publishing, Cham, pp. 253–266. [https://doi.org/10.1007/978-3-](https://doi.org/10.1007/978-3-319-96175-0_12)
11 [319-96175-0_12](https://doi.org/10.1007/978-3-319-96175-0_12)
- 12 Lefèvre, F., Forget, F., 2009. Observed variations of methane on Mars unexplained by known
13 atmospheric chemistry and physics. *Nature* 460, 720–723.
14 <https://doi.org/10.1038/nature08228>
- 15 Lellouch, E., Encrenaz, T., de Graauw, T., Erard, S., Morris, P., et al., 2000. The 2.4–
16 spectrum of Mars observed with the infrared space observatory. *Planet. Space Sci.* 48,
17 1393–1405. [https://doi.org/10.1016/S0032-0633\(00\)00118-5](https://doi.org/10.1016/S0032-0633(00)00118-5)
- 18 Liuzzi, G., Masiello, G., Serio, C., Venafrà, S., Camy-Peyret, C., 2016. Physical inversion of
19 the full IASI spectra: Assessment of atmospheric parameters retrievals, consistency of
20 spectroscopy and forward modelling. *J. Quant. Spectrosc. Radiat. Transf.* 182, 128–
21 157. <https://doi.org/10.1016/j.jqsrt.2016.05.022>
- 22 Liuzzi, G., Villanueva, G.L., Crismani, M.M.J., Smith, M.D., Mumma, M.J., et al., 2020.
23 Strong Variability of Martian Water Ice Clouds During Dust Storms Revealed From
24 ExoMars Trace Gas Orbiter/NOMAD. *J. Geophys. Res. Planets* 125.
25 <https://doi.org/10.1029/2019JE006250>
- 26 Liuzzi, G., Villanueva, G.L., Mumma, M.J., Smith, M.D., Daerden, F., et al., 2019. Methane
27 on Mars: New insights into the sensitivity of CH_4 with the NOMAD/ExoMars
28 spectrometer through its first in-flight calibration. *Icarus* 321, 671–690.
29 <https://doi.org/10.1016/j.icarus.2018.09.021>
- 30 Lyons, J.R., 2005. Formation of methane on Mars by fluid-rock interaction in the crust.
31 *Geophys. Res. Lett.* 32, L13201. <https://doi.org/10.1029/2004GL022161>
- 32 Maguire, W.C., 1977. Martian isotopic ratios and upper limits for possible minor constituents
33 as derived from Mariner 9 infrared spectrometer data. *Icarus* 32, 85–97.
34 [https://doi.org/10.1016/0019-1035\(77\)90051-3](https://doi.org/10.1016/0019-1035(77)90051-3)
- 35 Mangold, N., Baratoux, D., Witasse, O., Encrenaz, T., Sotin, C., 2016. Mars: a small
36 terrestrial planet. *Astron. Astrophys. Rev.* 24, 15. [https://doi.org/10.1007/s00159-016-](https://doi.org/10.1007/s00159-016-0099-5)
37 [0099-5](https://doi.org/10.1007/s00159-016-0099-5)
- 38 Moores, J.E., Gough, R.V., Martinez, G.M., Meslin, P.-Y., Smith, C.L., et al., 2019a.
39 Methane seasonal cycle at Gale Crater on Mars consistent with regolith adsorption
40 and diffusion. *Nat. Geosci.* 12, 321–325. <https://doi.org/10.1038/s41561-019-0313-y>
- 41 Moores, J.E., King, P.L., Smith, C.L., Martinez, G.M., Newman, C.E., et al., 2019b. The
42 Methane Diurnal Variation and Microseepage Flux at Gale Crater, Mars as
43 Constrained by the ExoMars Trace Gas Orbiter and Curiosity Observations. *Geophys.*
44 *Res. Lett.* 46, 9430–9438. <https://doi.org/10.1029/2019GL083800>
- 45 Moores, J.E., Schuerger, A.C., 2012. UV degradation of accreted organics on Mars: IDP
46 longevity, surface reservoir of organics, and relevance to the detection of methane in
47 the atmosphere: ORGANIC IDP SURFACE CARBON ON MARS. *J. Geophys. Res.*
48 *Planets* 117, n/a-n/a. <https://doi.org/10.1029/2012JE004060>
- 49 Mumma, M.J., Novak, R.E., Bonev, B.P., DiSanti, M.A., 2003. A sensitive search for
50 methane on Mars. Presented at the American Astronomical Society, Bulletin of the

- 1 American Astronomical Society.
- 2 Mumma, M.J., Villanueva, G.L., Novak, R.E., Hewagama, T., Bonev, B.P., et al., 2009.
- 3 Strong Release of Methane on Mars in Northern Summer 2003. *Science* 323, 1041–
- 4 1045. <https://doi.org/10.1126/science.1165243>
- 5 Neefs, E., Vandaele, A.C., Drummond, R., Thomas, I.R., Berkenbosch, S., et al., 2015.
- 6 NOMAD spectrometer on the ExoMars trace gas orbiter mission: part 1—design,
- 7 manufacturing and testing of the infrared channels. *Appl. Opt.* 54, 8494.
- 8 <https://doi.org/10.1364/AO.54.008494>
- 9 Oehler, D.Z., Etiope, G., 2017. Methane Seepage on Mars: Where to Look and Why.
- 10 *Astrobiology* 17, 1233–1264. <https://doi.org/10.1089/ast.2017.1657>
- 11 Olsen, K.S., Lefèvre, F., Montmessin, F., Trokhimovskiy, A., Baggio, L., et al., 2020. First
- 12 detection of ozone in the mid-infrared at Mars: implications for methane detection.
- 13 *Astron. Astrophys.* 639, A141. <https://doi.org/10.1051/0004-6361/202038125>
- 14 Rodgers, C.D., 2000. *Inverse Methods for Atmospheric Sounding: Series on Atmospheric,*
- 15 *Oceanic and Planetary Physics.* World Scientific Publishing Co. Pte. Ltd.
- 16 Roos-Serote, M., Atreya, S.K., Webster, C.R., Mahaffy, P.R., 2016. Cometary origin of
- 17 atmospheric methane variations on Mars unlikely: METHANE ON MARS AND
- 18 COMETS UNCORRELATED. *J. Geophys. Res. Planets* 121, 2108–2119.
- 19 <https://doi.org/10.1002/2016JE005076>
- 20 Segura, A., Navarro-González, R., 2005. Production Of Low Molecular Weight
- 21 Hydrocarbons By Volcanic Eruptions On Early Mars. *Orig. Life Evol. Biospheres* 35,
- 22 477–487. <https://doi.org/10.1007/s11084-005-6420-3>
- 23 Smith, M.D., 2019. THEMIS Observations of the 2018 Mars Global Dust Storm. *J. Geophys.*
- 24 *Res. Planets* 124, 2929–2944. <https://doi.org/10.1029/2019JE006107>
- 25 Smith, M.D., 2008. Spacecraft Observations of the Martian Atmosphere. *Annu. Rev. Earth*
- 26 *Planet. Sci.* 36, 191–219. <https://doi.org/10.1146/annurev.earth.36.031207.124334>
- 27 Summers, M.E., Lieb, B.J., Chapman, E., Yung, Y.L., 2002. Atmospheric biomarkers of
- 28 subsurface life on Mars: ATMOSPHERIC BIOMARKERS ON MARS. *Geophys.*
- 29 *Res. Lett.* 29, 24-1-24-4. <https://doi.org/10.1029/2002GL015377>
- 30 Thomas, I.R., Vandaele, A.C., Robert, S., Neefs, E., Drummond, R., et al., 2016. Optical and
- 31 radiometric models of the NOMAD instrument part II: the infrared channels - SO and
- 32 LNO. *Opt. Express* 24, 3790. <https://doi.org/10.1364/OE.24.003790>
- 33 Trokhimovskiy, A., Perevalov, V., Korablev, O., Fedorova, A.F., Olsen, K.S., et al., 2020.
- 34 First observation of the magnetic dipole CO₂ absorption band at 3.3 μm in the
- 35 atmosphere of Mars by the ExoMars Trace Gas Orbiter ACS instrument. *Astron.*
- 36 *Astrophys.* 639, A142. <https://doi.org/10.1051/0004-6361/202038134>
- 37 Vandaele, A.C., Korablev, O., Daerden, F., Aoki, S., Thomas, I.R., et al., 2019. Martian dust
- 38 storm impact on atmospheric H₂O and D/H observed by ExoMars Trace Gas Orbiter.
- 39 *Nature* 568, 521–525. <https://doi.org/10.1038/s41586-019-1097-3>
- 40 Vandaele, A.C., Lopez-Moreno, J.-J., Patel, M.R., Bellucci, G., Daerden, F., et al., 2018.
- 41 NOMAD, an Integrated Suite of Three Spectrometers for the ExoMars Trace Gas
- 42 Mission: Technical Description, Science Objectives and Expected Performance.
- 43 *Space Sci. Rev.* 214, 80. <https://doi.org/10.1007/s11214-018-0517-2>
- 44 Vandaele, A.C., Neefs, E., Drummond, R., Thomas, I.R., Daerden, F., et al., 2015. Science
- 45 objectives and performances of NOMAD, a spectrometer suite for the ExoMars TGO
- 46 mission. *Planet. Space Sci.* 119, 233–249. <https://doi.org/10.1016/j.pss.2015.10.003>
- 47 Villanueva, G.L., Liuzzi, G., Crismani, M.M.J., Aoki, S., Vandaele, A.C., et al., 2020. Strong
- 48 isotopic fractionation observed in the Martian atmosphere with ExoMars/NOMAD.
- 49 *Sci. Adv.*
- 50 Villanueva, G.L., Mumma, M.J., Novak, R.E., Radeva, Y.L., Käufel, H.U., et al., 2013. A

1 sensitive search for organics (CH₄, CH₃OH, H₂CO, C₂H₆, C₂H₂, C₂H₄),
2 hydroperoxyl (HO₂), nitrogen compounds (N₂O, NH₃, HCN) and chlorine species
3 (HCl, CH₃Cl) on Mars using ground-based high-resolution infrared spectroscopy.
4 *Icarus* 223, 11–27. <https://doi.org/10.1016/j.icarus.2012.11.013>

5 Villanueva, G.L., Smith, M.D., Protopapa, S., Faggi, S., Mandell, A.M., 2018. Planetary
6 Spectrum Generator: An accurate online radiative transfer suite for atmospheres,
7 comets, small bodies and exoplanets. *J. Quant. Spectrosc. Radiat. Transf.* 217, 86–
8 104. <https://doi.org/10.1016/j.jqsrt.2018.05.023>

9 Viscardy, S., Daerden, F., Neary, L., 2016. Formation of layers of methane in the atmosphere
10 of Mars after surface release: FORMATION OF LAYERS OF METHANE ON
11 MARS. *Geophys. Res. Lett.* 43, 1868–1875. <https://doi.org/10.1002/2015GL067443>

12 Waugh, D.W., Toigo, A.D., Guzewich, S.D., 2019. Age of martian air: Time scales for
13 martian atmospheric transport. *Icarus* 317, 148–157.
14 <https://doi.org/10.1016/j.icarus.2018.08.002>

15 Webster, C.R., Mahaffy, P.R., 2011. Determining the local abundance of Martian methane
16 and its ¹³C/¹²C and D/H isotopic ratios for comparison with related gas and soil
17 analysis on the 2011 Mars Science Laboratory (MSL) mission. *Planet. Space Sci.* 59,
18 271–283. <https://doi.org/10.1016/j.pss.2010.08.021>

19 Webster, C.R., Mahaffy, P.R., Atreya, S.K., Flesch, G.J., Farley, K.A., et al., 2013. Low
20 Upper Limit to Methane Abundance on Mars. *Science* 342, 355–357.
21 <https://doi.org/10.1126/science.1242902>

22 Webster, C.R., Mahaffy, P.R., Atreya, S.K., Flesch, G.J., Malespin, C.A., et al., 2020.
23 Curiosity Mars methane measurements are not confused by ozone. *Astron. Astrophys.*
24 641, L3. <https://doi.org/10.1051/0004-6361/202038815>

25 Webster, C.R., Mahaffy, P.R., Atreya, S.K., Flesch, G.J., Mischna, M.A., et al., 2015. Mars
26 methane detection and variability at Gale crater. *Science* 347, 415–417.
27 <https://doi.org/10.1126/science.1261713>

28 Webster, C.R., Mahaffy, P.R., Atreya, S.K., Moores, J.E., Flesch, G.J., et al., 2018.
29 Background levels of methane in Mars' atmosphere show strong seasonal variations.
30 *Science* 360, 1093–1096. <https://doi.org/10.1126/science.aag0131>

31 Wong, A.-S., 2003. Chemical markers of possible hot spots on Mars. *J. Geophys. Res.* 108,
32 5026. <https://doi.org/10.1029/2002JE002003>

33 Yung, Y.L., Chen, P., Nealson, K., Atreya, S., Beckett, P., et al., 2018. Methane on Mars and
34 Habitability: Challenges and Responses. *Astrobiology* 18, 1221–1242.
35 <https://doi.org/10.1089/ast.2018.1917>

36 Zahnle, K., 2015. Play it again, SAM. *Science* 347, 370–371.
37 <https://doi.org/10.1126/science.aaa3687>

38 Zahnle, K., Freedman, R.S., Catling, D.C., 2011. Is there methane on Mars? *Icarus* 212, 493–
39 503. <https://doi.org/10.1016/j.icarus.2010.11.027>

40