Investigation on the Absorption Bands Around 3.3 μm in CRISM Data

Paola Manzari (✉ paola.manzari@est.asi.it)

Agenzia Spaziale Italiana <https://orcid.org/0000-0002-2952-3660>

Cosimo Marzo

Agenzia Spaziale Italiana

Eleonora Ammannito

Agenzia Spaziale Italiana

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Abstract

Recently, the methane seepage detected by Mars Sample Laboratory (MSL) in the Gale crater area during 2013 was confirmed by methane detection by the Planetary Fourier Spectrometer (PFS). While analyzing NIR-IR CRISM data on a site in Oxia Planum area, in the view of a future comparison with data that will be collected by the Rosalind Franklin rover onboard the ExoMars2022 mission, a 3.3 μm absorption was noted in some pixel spectra. Since methane, like other hydrocarbons, shows absorptions in the range 3.1-3.6 μm , we begun to study this band in CRISM data to explore the possibility to look for seepages on Mars surface. The datasets chosen for this study, aside the site in Oxia Planum area, include some sites of observations on Gale Crater and other sites in Nili Fossae area. We used the Planetary Spectrum Generator to simulate CRISM spectra of the different sites, with the diverse concentrations of CH_4 spikes. These simulations served to establish the relation between concentration and methane band depths, as seen by CRISM spectrometer. Then, mapping the Modified Gaussian Model fit on CRISM data, we extracted the band parameters of the absorptions in the 3.3 μm spectral region. Aside rare, suspected absorptions, an artifact was highlighted. Therefore, we have set a threshold on the depth to consider as depth of potential true absorptions, on the basis of the standard deviation (σ) of absorption depth map. Finally, we concluded to favor as potential absorptions: distribution of clusters of pixels in the band mapping not vertically stacked and a threshold value $>\mu$ (average) + 5σ (standard deviation) of the depth map. These threshold values set the lower limit for each observation on the methane concentration potentially detectable by CRISM. The threshold value varies from one observation to another, in a range between 0.0136-0.0237, that would correspond in a range of lower limit concentrations of 180 and 600 ppbv. We found interesting cluster of pixels which spectra overcome the imposed threshold. We still consider that part of them could still be a kind of unknown artifact. Nevertheless, the aim of this paper is to show that CRISM data can show potential absorptions of methane in such quantities that in some observations are compatible with the order of the methane spikes effectively detected in literature. Even if this work does not confirm nor deny the occurrences of methane seepages in the investigated images it shows a possible method for assessing a confidence limit in the detection of this band in CRISM data.

Introduction

The great part of the missions on Mars is focused on the research of past/present life on the Mars surface and subsurface. In these last ten years a number of steps forward have been made in the knowledge of Mars environments that could constitute proxies for the development of primitive lifeforms. In this sense, the findings related to methane continue to be intriguing because on the Earth, part of it, formed by microbes from the domain Archaea in anoxic conditions during the Proterozoic age (Pavlov et al., 2003). Nevertheless, methane, like other hydrocarbon compounds, can result from abiogenic geological processes (Etiope et al., 2011, 2013). For the methane gas these can be serpentinization of basalts, (Oze and Sharma, 2005), gas absorbed in the regolith (Meslin et al., 2010; Gough et al., 2010) or geothermal processes (Etiope et al., 2011), release from subsurface clathrates Chassefière, (2009).

To date, several instruments both orbiting and onboard rovers have detected methane on Mars surface. Since 2003, several puzzling detections of methane in the Mars atmosphere were done (Atreya et al., 2007). For example, from Earth: using the Cryogenic Near-IR Facility Spectrograph (CSHELL) at the Infrared Telescope Facility (IRTF) and the Gemini ground telescopes, Mumma et al., (2004), detected localized points with > 250 ppbv of methane, a concentration that was then corrected at 45 ppbv, comparing data with PFS measurements (Mumma et al., 2009). The Fourier Transform Spectrometer (FTS) at Canada-French-Hawaii Telescope (CFHT) measured 10 ppbv, (Krasnopolsky et al., 2004). From Mars, through the Planetary Fourier Spectrometer on board the Mars Express mission, Formisano et al., (2004) obtained a methane concentration around 10 ppbv.

Therefore, looking also at the successive measurements from 2003, a distinction has to be made for what concerns methane detection on Mars: background detections in atmosphere and detection of “spikes” and “plumes” of methane which differ by orders of magnitude in ppb of concentration.

For what concerns quantitative measurements of methane background, some months ago, Korablev et al., (2019), looking at the first measurements of the Exomars 2016 Trace Gas Orbiter (TGO), which works in solar occultation, provided an upper limit of methane in the atmosphere above 5 km of < 0.05 ppbv. Instead, the 3 years measurements of Mars Surface Laboratory (MSL)-Tunable Laser Spectrometer (TLS) onboard Curiosity found a background mixing ratio value in Gale crater of 0.2–0.6 ppbv (Webster et al., 2015, 2018) near the surface at night. To fillet these two measurements Moorees et al. (2019), hypothesized a diurnal cycle for methane in which it is essentially diluted during the martian day for the effect of currents convection, thus justifying the methane abundance found by TGO. During the night the Planetary Boundary Layer (PBL) drastically fall and diffusivity of the Martian atmosphere with it (Guzevich et al., 2017), making possible for the surface to “keep” small quantities of methane.

For what concerns spikes: the detection of Mumma et al., (2009), that observed a strong release of methane up to 50 ppbv during the Northern Hemisphere summer of 2003. Their observations ranged up to 3 years in which they observed a progressive decreasing in the methane mixing ratio over the three years and a substantial variation according to latitude. They concluded that the occurring of this strong release of methane was limited spatially and temporarily.

Later, other spatial-temporal investigations with other instruments confirmed this conclusion.

Using the measurements of the Mars Express Planetary Fourier Spectrometer, (MEX-PFS) in spot tracking mode Giuranna et al., (2019), exploited successfully the chance of finding in the atmosphere an increase of methane just the terrestrial day after the first methane spike detection from the surface by Curiosity on 15 June 2013. The amount of methane detected by PFS was about 15 ppbv vs the 9 ppbv detected by the SAM-TLS (Webster et al., 2015). The last detection of a methane spike was done by the Sample Analysis at Mars (SAM-TLS) onboard the Curiosity rover, in 19 June 2019, measuring an abundance of methane never detected before by a rover, i.e. around 21 ppbv (Announced during the AbSciCon 24–28 June 2019).

All these findings provide interesting constraints on the occurrence of methane on Mars.

In fact, summarizing the results of the previous observations, the source of Mars methane should be spatially restricted but also temporarily restricted with potential sources in form of seepages (Yung et al., 2018): from micro-seepages, (Etiope et al., 2015; Moores et al., 2019), mini-seepages (Etiope et al., 2015) to macro-seepages, (Oehler et al., 2017). Furthermore, the different amounts detected in spikes Table 1, seasonal oscillations and non-detections are compatible with geological seepage dynamics that involve changes in gradient of pressure and in the permeability of rocks (Etiope and Oehler, 2019).

The variability of the amount of methane observed in these measurements and the estimated time for methane sequestration by photochemistry and oxidation that spans from months to years (Mumma et al., 2009), allow to hypothesize also that the plume release observed was recent at the time of the measurements.

Since the seasonal and local variation of the amount of methane suggests that the seepages could have an extension of meter to km scale, in this work, we explored the chance to find clues of C-H compounds in data of CRISM. In fact, hydrocarbons show absorptions in the IR range between 3.1 and 3.6 μm and CRISM has an IR range up to 3.92 μm with a spatial resolution capable of investigating the surface at a tens meter scale.

Different studies such as Clark et al., (2009) and Kaplan (2016), Sadjadi et al., (2018) found that organic compounds of which hydrocarbons represent the main group, show strong absorptions in the NIR range around 2.3 and IR range around 3.3 μm . Absorptions at longer wavelengths (3.3–3.6 μm) are characteristics of aliphatic compounds whereas between 3.1 and 3.3 μm feature the absorptions of aromatic compounds Kaplan (2016).

Diverse remote hyperspectral systems have detected absorptions in these ranges on planetary surfaces for example: VIR on Ceres detected several features in a range between 3.3 to 3.6 μm spectral range characteristic of stretching modes of methyl (CH_3) and methylene (CH_2) functional groups (De Sanctis et al., 2017).

At 3.3 μm , beside hydrocarbons, Villanueva et al., (2008) discovered a band system of isotopic CO_2 (carbon dioxide) using data from space and ground-based telescopes. Furthermore, also CO_2 ice shows a strong absorption at 3.3 μm (Hansen et al., 1997). However, the phase diagram of CO_2 for Mars shows that at average temperatures around -50°C , at average latitudes, and pressure around 6 millibar, CO_2 should be present in gas form (Longhi 2006). This research focused on signatures of hydrocarbons in the IR range on the surface of Mars. Oehler and Etiope, 2017, point out that due to the transient nature of the methane detected on Mars and the uncertainty on its lifetime in the Martian atmosphere, the only method for studying methane seepages on Mars surface is placing probes on the ground at fixed positions. This would allow constant sampling of the gas methane to determine fluxes and for minimizing the effects of isotopic fractionation of CH_4 which is important to ascend to its origin. However, if macro seepages could be, at first, localized from remote sensing data, it would be possible to plan a landing mission for taking ground instruments and measuring methane fluxes directly on these macro seep sources.

Therefore, we started this work to search potential methane spikes with these premises:

- 1) In June 2019, estimated CH₄ abundance on Mars surface is about 20 ppbv by SAM-TLS (AbSciCon 24–28 June 2019), and it is unknown the distance of Curiosity from the source of the detected spike.
- 2) Detection of plumes from ground telescopes during 2003 of about 40 ppbv (Mumma et al., 2004, 2009) were integrated on a wide area. We hypothesize that this abundance on a broad area would potentially mean a greater concentration in the source sites.
- 3) The time of survival of CH₄ in atmosphere spans from hours to 3 hundred years (Dartnell et al., 2012).
- 4) Since August 2012, Curiosity detected only two methane spikes during 2013 and 2019. Assuming that these sudden increases of methane concentration are sporadic, in our work, we were looking for CH₄ absorption that eventually would correspond to spikes of CH₄ in the scene, i.e. a concentration of methane greater than the values found for the background of some tens/hundreds of ppb. Consequently, we expected to find eventually few featured pixels/none in the greater part of the investigated images.

Literature data related to methane showed that a background does exist due to probable seepages that could be activated by different processes (Etiope and Oehler, 2019; Oehler and Etiope, 2017; Korablev et al., 2019; Webster et al., 2015, 2018).

Beside methane, the feature at 3.3 μm is also typical of other more complex C-H compounds, the Polycyclic Aromatic Hydrocarbons (PAH), (Tokunga et al., 1991). Like methane, also PAH's can be originated by degradation of organisms (Mckay and Gibson, 1996). In this case, the eventual detection would be related to the time of the single observation with lower chances to find them again in eventual missions. This, for two reasons: nature of PAH's which origins and eventual relation with the environment could be only studied by in situ chemical facilities, and due to the short time, about 3 days, (Dartnell et al., 2012) of surviving of PAH's exposed at UV rays on surface.

Moreover, also ethane shows absorptions at 3.3 μm , but the only data are from Krasnopolsky, (2011), with IRTF-CSHELL that placed an upper limit of ethane in Mars atmosphere of 0.3 ppb. It is similar to background values of methane concentration on Mars surface. We did not search, nor expect to detect spectral features in 3.3 μm region at such concentrations.

Table 1

List of the Mars sites in which methane increases were observed by means of ground telescopes and spectrometers both orbiting (PFS) and on the Mars surface laboratory (MSL). Acronyms: Cryogenic Near-IR Facility Spectrograph (CSHELL) - Infrared Telescope Facility (IRTF); NIRSPEC, cross-dispersed echelle spectrograph designed for Keck II; Sample Analysis at Mars- Tunable Laser Spectrometer (SAM-TLS).

Methane spikes detection						
Area	Sensor	UTC	Solar Longitude, Ls, degree	Season	CH ₄ mixing ratio (ppbv)	Reference
Terra Sabae, Nili Fossae, SE-Syrtis Major	CSHELL/IRTF, NIRSPEC/Keck-2	12 Jan 2003	122	Northern Hemisphere Summer	40ppbv	Mumma et al., 2009
		18–19 Mar 2003	155			
Gale Crater	SAM-TLS	16 Jun 2013	336	Northern Hemisphere Winter-End of dust season	6-10ppbv	Webster et al., 2015
	PFS				15ppbv	
						Giuranna et al., 2019
Gale Crater	SAM-TLS	19 Jun 2019	41	Northern Hemisphere Spring	21ppbv	Curiosity team, 2019

Data And Methods

The scope of this work is to search in hyperspectral data acquired by CRISM over selected areas spectral absorptions that can be linked to the presence of methane. To this end, the considered CRISM cubes are processed to obtain the map of 3.3 μm absorption depth, center, and width. Afterwards, the spectra with potentially true absorptions are selected, based on the statistics of the depth map at 3.3 μm and excluding those pixels clearly related to artifacts. Finally, we did a simulation with Planetary Spectrum Generator (PSG) tool to obtain a relation that links spectral properties (*i.e.* absorption depth) to CH₄ concentrations.

Areas Selection

We considered three areas: area of Oxia Planum, in the view of the upcoming Exomars 2022 mission (Vago et al., 2017), to compare the results of this work with data collected on Martian surface by the Rosalind Franklin rover (Voosen, 2017); area of Gale crater in which the increase of methane was proven from orbiter and on ground; area of Nili Fossae which mineralogy is compatible with methane formation

(Wray and Elhmann, 2011) and in which the abundance 40 ppbv of methane was estimated from ground telescopes (Mumma et al., 2009). The three areas chosen for the research are indicated with stars in Fig. 1.

CRISM data processing

CRISM is a hyperspectral imaging spectrometer on the Mars Reconnaissance Orbiter (MRO) that collects images in a spectral range from 0.4 to 4 μm , (Murchie et al., 2007a). It operates in two modes: (1) a 72-channel mapping mode that provide global coverage at 200 m/pixel and (2) a full 544-channel targeted mode that provides a resolution of 15–38 m/pixel. For this study, we used full resolution targeted observations –FRS and FRT- which have a spatial resolution of about 20 m/pixel; Half-Resolution Long and Short Targeted observations (HRL-HRS) which have a spatial resolution of 36 m/pixel; Along-Track Undersampled (ATU) observations which have a resolution of 18 m/pixel cross-track and 36 m/pixel downtrack.

For each area the CRISM observations considered are listed in table 2.

Table 2
Observation season. List of the investigated CRISM observations (frs, frt, atu, hrs, hrl) and corresponding martian season of the observations.

<i>Area</i>	<i>CRISM-MRO observation</i>	<i>UTC</i>	<i>Solar Longitude, Ls, in degree</i>
Gale Crater	frs00028346	13 Jan 2013	243.7
	frt0000a091	20 Feb 2008	34.5
	frt00001968	21 Jun 2010	107.4
	hrs0000336a	30 Nov 2006	143.2
Oxia Planum	frs0003a896	23 Feb 2016	112.8
	frs00031523	21 Jul 2014	165.1
	frt00010fe9	11 Feb 2009	208
	atu0004180	5 Feb 2017	312
	hrl0000a3de	4 Mar 2008	40.3
	hrs00011725	5 Mar 2009	221.2
Nili Fossae	frs00041a28	14 Feb 2017	317.2
	frs0002a9b2	30 Jul 2013	359.6
	frs0002adc4	16 Aug 2013	7.7
	frs00039936	23 Dec 2015	85.2

The elaboration of CRISM data followed two processing chains: the first follows the steps implemented in the CRISM Analytical Toolkit (CAT) as a package in Envi software. This first kind of processing is necessary to remove atmospheric and photometric effects and to remove instrument artifacts. Specifically, the cubes are corrected in reflectance (I/F), (Murchie et al. 2007a, 2009b), then, I/F data are divided for the cosine of the solar incidence angle and finally the atmospheric contribution is removed using the so called Volcano Scan method. In the volcano scan method, an atmospheric transmission spectrum is derived from observations at the base and top of Olympus Mons (Mustard et al., 2005).

Processing of 3.3 μ m absorption

Then, for what concerns the peak around 3.3 μ m, another chain of processing was created. Each CRISM I/F cube was processed through a procedure that, as first, removes spectral spikes and results in a hyperspectral cube in which the range of I/F is between 0.0 and 0.3. After this step, a destriping process is applied according to the procedure described in De Angelis et al., 2015. This last processing undergoes another processing for searching the 3.3 μ m absorption.

For each pixel in the scene, only the portion of spectrum in the range between 3.2 and 3.4 is considered.

Since we are considering a narrow range the continuum was removed by subtracting a linear function passing through the reflectance value of the first and last point of the range.

After continuum removal, a Modified Gaussian Model (Sunshine, 1990) function was fitted to obtain the map of the absorption parameters: band center, depth, width, bias. A specific routine allows to set a threshold for each of the band parameters computed and to print those spectra within such threshold.

Noise estimation and choice of the thresholds

In CRISM data there are different sources of noise. In fact, there is the noise with a Poisson distribution characteristic of the VNIR S-detector and IR L-detector, and thermal noise which characterizes the IR-L detectors (Murchie et al., 2007; Kreisch et al, 2017). In particular, the degradation over time of the cryogenic cooler of L detector generated an increase of the noise in CRISM scenes (Murchie et al., 2007). Moreover, CRISM data can show vertical striping due to misfit in the calibration of detectors. Finally, a stochastic noise can occur as spectral spikes that are related to brusque change in brightness (Leask et al., 2018).

In order to find the detection limit of methane concentration in CRISM data we calculated the statistics of depth values on the absorption map in the range between 3.2 and 3.4 μ m. To take into account all the noise sources and the variability of the different CRISM scenes considered for this work, the standard deviation must be calculated for every observation.

Since in the images there are unknown artifacts, for each image, a threshold was set at $\mu + n \cdot \sigma$, where μ and σ are respectively, the average value and the standard deviation of depth map. From the analyses of data, we found that value of $n = 5$ for σ is a good compromise for avoiding false positives. This threshold

on the 3.3 μm depth set the lower concentration limit for detection of methane through CRISM in real data.

Mars surface modeling

In order to see if the estimated quantities of methane by literature data would be observable by CRISM we used the Planetary Spectrum Simulator (PSG). The PSG for surface modeling using CRISM data combines a realistic Hapke scattering model and the capability to ingest a broad range of optical constants allowing to accurately compute surface reflectances and emissivities (Villanueva et al., 2018). To simulate spectra of Mars surface for each CRISM observation, the PSG tool requests some parameters: date and season of the observation, the position of target and the geometry of the view, the atmosphere and surface properties, the characteristics of the observing instrument, such as altitude of observation, spectral range and resolution. The noise was not simulated but directly computed on each CRISM observation.

Through the PSG tool, simulating each CRISM observation, we found the relation between increasing methane concentration and the band depth at 3.3 μm . Then, using CRISM data, we have converted the calculated threshold on depth into lower limits of methane detection, for each observation.

Results

Spectral investigation on CRISM I/F observations

Using the procedure that calculates the Modified Gaussian Model fit (MGM), (Sunshine et al., 1999) on the CRISM I/F observations, the research of band minima in 3.2-3.4 μm range highlighted artifacts that create false absorptions (artefact absorptions from now, on) in some pixels that were distributed along the columns direction. For example, in fig. 2a the observation frs0002a9b2 is considered. The map of the band depth at 3.3 μm of this image shows the spatial distribution of cluster of pixels along columns. The fig. 2c shows the spectrum of one pixel in this cluster.

Through the investigated data we found that the position of artefact absorption is variable spatially and spectrally between 3.34 and 3.4 μm . To avoid false positives, we considered only those pixels in clusters that did not show a distribution along the columns of the images. Despite this precaution, there might still be false positives in the selected pixels.

In table 3, for each selected cluster, we listed the x, y coordinate of pixels with highest value of the depth, band center the number of the pixel the average value (μ), and standard deviation (σ) of depth of the cluster.

In figures 3,4,5 there are the results of the band minima in the range of 3.2-3.4 for three sites in three investigated areas. In the observation frs0003a896, the depth of the deeper pixel in the cluster (red fig. 3) is -0.0123 with a band center at 3.34 μm .

In the observation frs00028346, the depth of the deepest pixel in the cluster (red fig. 4) is -0.0200 with a band center at 3.35 μm .

In fig. 5 the image frs0002a9b2 is shown. Red pixels indicate the 3.297 μm absorption. The maximum value of absorption depth in the red cluster is 0.045.

Table 3

List of the pixels that show features in the range 3.2-3.4 μm . The pixels belong to clusters, but the x,y coordinates are referred to the pixel with the greater depth. μ, σ are respectively, the average value and the standard deviation of depth map.

<i>Area</i>	<i>CRISM-MRO observation</i>	<i>Coordinate of the deepest pixel in the cluster</i>	<i>Band center</i>	<i>Depth</i>	<i>N of pixels in the cluster</i>	<i>μ, σ of the cluster</i>
Gale Crater	frs00028346	x355y88	3.35	-0.022	5	-0.009, 0.007
	frt0000a091	-	-	-	-	-
	frt00001968	x121y106	3.35	-0.057	5	-0.05, 0.007
	hrs0000336a	-	-	-	-	-
Oxia Planum	frs0003a896	x420y133	3.29	-0.024	6	-0.002, 0.005
	frs00031523	x459y165	3.32	-0.040	7	-0.03, 0.013
	frt00010fe9	x120y139	3.31	-0.032	5	-0.03, 0.007
	atu0004180	x345y172	3.28	-0.036	8	-0.03, 0.007
	hrl0000a3de	-	-	-	-	-
Nili Fossae	hrs00011725	x182y8	3.29	-0.023	5	-0.17, 0.003
	frs00041a28	x506y22	3.37	-0.042	6	-0.03, 0.007
	frs0002a9b2	x47y3	3.29	-0.045	15	-0.044, 0.005
	frs0002adc4	-	-	-	-	-
	frs00039936	x135y49	3.29	-0.013	4	-0.013, 0.0005

Statistics of clusters

Next, to establish a threshold for the depth, we computed the average μ and the standard deviation σ of the depth map of absorptions in the 3.3 μm region, for each dataset.

For each image, the average depth value ranged from - 0.01 to -0.003 and the standard deviation of depth maps resulted from 0.002 to 0.004, Table 4.

Therefore, we have considered as threshold for potential absorptions only depth values greater than $\mu + 5\sigma$, for each image. Within the considered dataset, the resulting threshold values range from 0.0136 to 0.0237.

Table 4

Threshold estimation for each site. In this table, the thresholds for each site and corresponding quantification, according to PSG simulation.

<i>Area</i>	<i>CRISM-MRO observation</i>	<i>Number of pixels in depth map</i>	<i>Standard deviation on depth map (σ)</i>	<i>Average (μ)</i>	<i>Threshold $\mu + 5\sigma$</i>	<i>Lower limit of concentrations</i>
Gale Crater	frs00028346	84475	0.003	-0.0055	0.0205	300
	frt0000a091	228660	0.003	-0.005	0.02	350
	frt00001968	221400	0.004	-0.007	0.027	600
	hrs0000336a	51940	0.002	-0.01	0.02	400
Oxia Planum	frs0003a896	83550	0.002	-0.005	0.015	220
	frs00031523	73920	0.003	-0.004	0.019	350
	frt00010fe9	228900	0.003	-0.006	0.021	300
	atu0004180	91575	0.003	-0.003	0.018	280
	hrl0000a3de	112518	0.004	-0.0037	0.0237	320
	hrs00011725	51900	0.002	-0.005	0.015	200
	frs00041a28	82500	0.003	-0.0036	0.0186	180
Nili Fossae	frs0002a9b2	90234	0.002	-0.004	0.014	210
	frs0002adc4	87920	0.002	-0.0036	0.0136	200
	frs00039936	79750	0.002	-0.004	0.014	200

Simulated spectrum of methane gas on Mars surface

The simulation of surface spectra plus increasing content of methane (in ppbv) was computed by the Planetary Spectrum Generator (PSG) tool using different parameters depending on the position respect to the Sun of the investigated CRISM observation site. The use of PSG simulator was intended to estimate the empirical function that link absorption depths, as they would be detected by CRISM, to methane abundances.

As an example, the simulated I/F spectrum, in the 3.2–3.8 μm range of the observation frs0003a896, in Oxia Planum area, shows a weakly visible band absorption at 3.3 μm (Fig. 6) corresponding to the CH₄ input value of 100 ppbv. To study how the band can vary in depth according to different concentrations we also simulated: 40, 100, 300, 500 ppbv (Fig. 7) and plot the corresponding depth for each area investigated (Fig. 8, 9, 10). The depth values are calculated as the depth of the minima in the spectrum absorption in the range 3.2–3.4 μm .

As seen, each CRISM observation of this work is collected during a different year, season and time (Table 2, Fig.11). However, the three plots of the increasing simulated CH₄ band absorption *vs* depth in the simulated spectra, show a general agreement among the depths, independently from the season and year of observation. Hence, in general, we can say that the depths of the absorption band at 3.3 μm of methane, would correspond to about 0.008 for 100 ppbv for all the sites. Only in the case of the observation frs00041a28, the concentration of 100 ppbv corresponds to a deeper value of absorption (depth=0.012).

Table 5

Overview table. Conversion from thresholds on 3.3 band depth to lower detection limit of methane concentration, according to PSG simulations.

<i>Area</i>	<i>CRISM-MRO observation</i>	<i>Threshold</i> <i>$\mu + 5\sigma$</i>	<i>Lower limit of concentrations</i>
Gale Crater	frs00028346	0.0205	300
	frt0000a091	0.02	350
	frt00001968	0.027	600
	hrs0000336a	0.02	400
Oxia Planum	frs0003a896	0.015	220
	frs00031523	0.019	350
	frt00010fe9	0.021	300
	atu0004180	0.018	280
	hrl0000a3de	0.0237	320
	hrs00011725	0.015	200
Nili Fossae	frs00041a28	0.0186	180
	frs0002a9b2	0.014	210
	frs0002adc4	0.0136	200
	frs00039936	0.014	200

In summary, we can say that looking at the plot of simulated observations (Fig. 8,9,10), the values of depths correspond to a range of methane concentration between 180 and 600 ppbv, depending on the considered site (Table 5).

Discussion

The simulations for each site (Fig. 8, 9, 10) show that the depths corresponding to same concentration of methane do not change much from site to site. For example, 100 ppbv corresponds to a range of depths from 0.008 to 0.012.

In these simulations, one exception is the observation frs00041a28 in Nili Fossae area which shows greater depths with respect to the other sites. This could be related to the viewing geometry or season/hour or a combination of these variables, see Fig. 12.

The depths of the deepest pixels in these featured clusters in CRISM observations show different values that goes from - 0.013 to -0.057 (Table 3).

To avoid, as more as possible, misinterpretation of false absorptions due to unknown artifacts the threshold for depth to consider was set at $\mu + 5\sigma$ of depth maps. The thresholds range from 0.0136 to 0.0237 (Table 4).

Comparing the plots of the simulated depths with the threshold derived from the depth map statistics, we could say that, for concentrations lower than 180–600 ppbv, depending on the considered site, would increase the chance to find a false absorption.

Good candidates but artefacts

Among the known artifacts of CRISM, there is an optical effect due to out of band leakage in zone 3 of the IR order sorting filter. This leakage peaks appears at 3.4 μm (Murchie et al., 2007). However, this kind of artifacts generates positive signal peaks.

However, we consider that absorptions or a great part of them could represent an unknown artifact. In fact, although we carefully analyzed the noise typical of each image, we have considered that these absorptions could be a new artifact similarly to a probable artifact found in CRISM data at 3.18 μm (Viviano-Beck et al., 2014). Furthermore, it could be another possible artifact, similar to ones found by Leask et al., (2018) named “spurious absorptions or absorption-like features”. This artifact consists of absorptions on over 20 channels, showing gradual shoulders from the continuum value. In our data, to exclude, at least, it was an artifact introduced from the I/F calibration, we analyzed radiance and I/F data, before the atmospheric correction. As it can be seen in the example of Fig. 12, the featured pixel of the image frs00029b2 shows the 3.3 absorption both in radiance spectrum and in I/F. Therefore, 3.3 μm absorption is not related to the I/F correction.

Good candidates, potential methane spikes?

Despite all the precautions, there is still the possibility that the feature identified is related with an artifact, however, some of the identified locations could indeed be localized methane sources. If some of the clusters were related to methane emissions, their findings would strengthen the hypothesis of localized sources of methane in the subsurface. In fact, data on Martian methane concentrations include background values (Webster et al., 2018), spikes (Mumma et al., 2009), non-detections (Korablev et al., 2019) and seasonality (Moore et al., 2018). The results of this investigation can well fit with sources of methane in form of gas seepages (Etiope and Oheler, 2019). In this work we find that if methane whiffs were present as emissions from gas seepages, in the selected dataset, CRISM could detect the methane spectral features for concentrations > 180–600 ppb, depending on the site.

Unfortunately, it is not possible to calculate the flux of this potential source, because CRISM does not collect data periodically in fixed areas, being conceived for studying the mineralogy of Mars surface. However, the clusters that satisfied the two criteria we set for potential methane detection in CRISM data,

consist of few pixels, 4–15. For each cluster, the value of the pixel with a deepest absorption is considered and listed in table 3. In general, the remaining pixels in the cluster show shallower absorptions. Which means that if these absorptions were methane, the clusters could represent diffusion of gas in the atmosphere from a source point, or a diffusion by a more spread source on the surface.

The concentrations found during this investigation are high respect to previous spikes and plumes detections, but remains in the order of hundreds of ppbv, also we do not have precise information regarding the time of methane removal/sinks from the atmosphere. In fact, the oxidation process on Mars destroys methane in about 300 years (Summers et al., 2002; Atreya et al., 2007). This mechanism is too long to explain, for example, the detection of the last spike of 21 ppbv by MSL (AbSciCon 24–28 June 2019) and the non-detection of Mars Express and ExoMars TGO (ESA's Mars orbiters did not see latest Curiosity methane burst; Korablev et al., 2019), after some hours on the same area.

Several hypotheses were formulated for a shorter lifetime of CH₄ that include gas-solids reactions, (Jensen et al., 2014; Holmes et al., 2015) however, the faster mechanism proposed for methane removal is the oxidation CH₄ by the action of hydrogen peroxide in the regolith (Lefevre and Forget, 2009). This mechanism could shorten the methane life from 200 days to few hours near the surface.

If in some of the featured pixels observed, the 3.3 μm band was due to increase of methane gas, then it would be one of the few detections of 3.3 μm by an imaging spectrometer. The imaging spectrometer VIMS onboard Cassini mission detected a strong deep band of methane at 3.3 μm on Titan's upper atmosphere. The estimation of abundance in this case was around 1.4% of the atmosphere (Maltagliati et al., 2014).

On the Earth, in 2010, a field experiment was performed at the former Rocky Mountain Oilfield Testing Center (RMOTC), Wyoming (USA), in which controlled flow rates of methane were released on surface and subsurface to simulate anthropogenic and natural sources. Simultaneously, the spectral imager on the SEBASS platform flew at 462 m and 762 m over these artificial sources of methane. The 3.3 μm band was detected on few pixels on surface and, in one station, also on the subsurface source (Scafutto et al., 2018).

Finally, very recently, the mid-infrared channel (MIR) of Atmospheric Chemistry Suite spectrometer onboard Trace Gas Orbiter (Korablev, et al., 2018) detected new bands in the range of methane absorptions, around 3.3 μm . These new bands were attributed to both ozone (Olsen et al., 2020) and to magnetic dipole and electric quadrupole 01111-00001 ($\nu_2 + \nu_3$) absorption bands of the main CO₂ isotopologue (Trokhimovskiy et al., 2020).

The spectral features we observed at 3.3 μm in CRISM data could be also assigned to magnetic dipole CO₂ absorption bands. Nevertheless, some of the differences between our investigation on CRISM data and ACS results stand in the geometry of the scene and location of investigations. The variation of latitude and geometry of the scene correspond also to variation in temperatures and pressures. In this work, we analyzed CRISM data acquired at Nadir whereas data from ACS were collected at solar

occultation conditions. Moreover, we focused the investigation on CRISM data at mid latitudes; the ACS spectrometer focused to northern latitudes ($> 65^{\circ}\text{N}$). However, currently, the new bands of ozone and CO₂ magnetic dipole are not integrated in the HITRAN database. Consequently, it is not possible to model the absorption of CO₂ and O₃ at 3.3 μm with the PSG tool.

Organic matter and PAH's

Some clusters that show absorptions at longer wavelengths, could be related to aliphatic hydrocarbons such as methane, as well as other aliphatic compounds that show absorptions at about 3.3–3.6 μm .

For example, aliphatic compounds were individuated in the spectral features of the comet 67P/Churyumov-Gerasimenko nucleus by VIRTIS spectrometer during the Rosetta mission (Raponi et al., 2020; Capaccioni et al., 2015).

Aliphatic features similar to kerite and asphaltite at 3.38 to 3.50 μm were found in the spectra of the crater Ernutet on Ceres asteroid by VIR spectrometer onboard Dawn mission.

Beside aliphatic compounds also aromatic hydrocarbons have been found in different planetary environments and materials. In particular, polycyclic aromatic hydrocarbons (PAHs) have been found in the organic fraction in carbonaceous chondrites (CCs) (Sephton et al. 1998; Botta and Bada 2002; Sephton 2002). Moreover, PAHs include up to 20% of the carbon material in the interstellar medium (ISM) (Allamandola et al. 1985). Signatures of PAHs have recently been identified in the atmosphere of Titan (López-Puertas et al., 2013).

Campbell et al., 2018 investigated on hydrocarbons detection on Mars South Polar Cap although the feature at 3.3 μm was difficult to interpret due to the strong absorption by the CO₂ ice, Oancea et al., 2012.

Even if studies (Dartnell et al., 2012; Pavlov et al., 2012) on Mars surface revealed a short lifetime and rapid degradation for PAH's in the shallow surface due to UV and ionizing radiations the eventual occasional occurrence of PAH's on surface images and the related 3.3 μm band absorption in CRISM data can be linked to PAH's bearing impacting bodies on Mars surface or in correspondence of fresh crater outcrops (Blanco et al., 2018).

Implications for ExoMars2022 and other rover missions

In 2022 the Exomars mission (Vago et al., 2017) will deliver the Kazachock surface platform and the Rosalind Franklin rover on Mars surface that will host several instruments onboard.

On the rover, almost all these instruments will provide data on eventual C-H compounds and organic molecules. Therefore, for what concerns Oxia Planum the results of this investigation would potentially be compared.

Once landed the rover, the Infrared Spectrometer for ExoMars (ISEM) will work coupled with the PanCam camera to select interesting sites for biosignatures. It has a spectral range of 1.15 to 3.3 μm with a spectral resolution 3.3 μm at 1.15 μm and 28 nm at 3.30 μm . As already seen, the range just end at the value of C-H absorption at 3.3 μm , therefore a potential comparison could be done, also looking for absorptions in the 2.2–2.4 μm range of C-H compounds. At micrometric scale, MicrOmega (Micro observatoire pour la minéralogie, l'eau, les glaces et l'activité) -IR will analyse *in situ* the powder material derived from crushed samples collected by the rover's core drill Ma_MISS. MicrOmega-IR has an IR range from 0.95 to 3.65 μm in 320 channels of about 8 nm of spectral resolution.

The analyses of samples collected in a depth up to 2 m by Ma_MISS will be very useful. In fact, either sample extracted will be not so much irradiated and damaged as the surface materials, and this increases the probability to find organic compounds. Moreover, in case of methane, this will be rapidly detected in the original abundance with respect to methane detected on the surface, which is mixed and/or removed from the Mars near surface atmosphere. This would be potentially possible, searching for other C-H absorptions at also in the region from 2.2 to 2.6 μm , range that is characterized by combination and overtone bands (Cloutis, 1989).

Finally, visible and NIR data on crushed samples will be compared with data from Raman Laser Spectrometer (RLS) that will permit the identification of minerals and the detection of different organic functional groups to be successively analyzed by the Mars Organic Molecules Analyzer (MOMA), (Rull et al., 2017). One of the major goals of the MOMA analyzer will be to assess whether the potential organic compounds detected are biogenic or abiogenic (Goetz et al., 2018).

Conclusions

The premises of this research were the following:

- 1) To June 2019, estimated CH_4 abundance on Mars surface is about 20 ppbv by SAM-TLS and is unknown the distance of Curiosity from the source of the detected spike.
- 2) Detection from ground telescopes in 2003 was around 40 ppbv, integrated on a great area.
- 3) According to literature, the time of survival of CH_4 in atmosphere spans from hours to 3 hundred years.
- 4) We were looking for CH_4 absorption that eventually would correspond to spikes of CH_4 in the scene, i.e. greater than the values found for the background of some tens/hundreds of ppb.
- 5) Consequently, in our research, we expected to find eventually few featured pixels/none in the greater part of the investigated images.

As results:

- In our work, by means of the Planetary Spectrum Generator (PSG) tool, (Villanueva et al., 2018) we found the relation that link the increasing methane to the depth of absorption at 3.3 μm , simulating with the PSG tool different amounts of CH_4 as would be viewed by CRISM.
- A procedure was created to map absorptions in the range 3.2-3.4 μm . This procedure automatically elaborates a chosen number of CRISM images: mapping the spectral parameters (MGM fitting for depth, band center, full width middle length) with a chosen threshold, and printing for each image the corresponding pixels, in order to rapidly finding them in the scene to be studied. The depth mapping showed an artifact recognizable by a distribution along columns of pixels. To exclude this artifact from interpretation, we chose two criteria for selecting potential C-H clusters: depth values $> m + 5 \cdot s$ of standard deviation of absorption depth in the 3.2-3.4 μm range and pixel clusters not clearly related to artifacts.
- Chosen this opportune thresholds for considering potential true absorptions and excluding vertical clusters, we found some clusters which absorptions can be related to C-H features, we discussed them as a new possible artifact and as potential C-H features.
- Different clusters were found in some locations of the three investigated areas. For Oxia Planum, the results of this study could be compared with the data on Mars surface from Exomars 2022.

Since CRISM is devoted to discovering the mineralogy of Mars surface and not for hydrocarbons detection, it does not collect data time to time, to monitor spectral changes in the same zone periodically.

Furthermore, the comparison with other instruments conceived to detect gas in atmosphere is difficult for different reasons: time of persistence of methane in Mars atmosphere (hours, months, years?), different spatial resolution and/or the non-correspondence of time of observations.

Due to artifacts and noise, in this work we cannot confirm the presence of methane seepages in the analyzed datasets. But neither we exclude that absorptions in some pixels can effectively be related to C-H compounds. Overall, we wanted to show a method to exploit CRISM data to search for C-H signatures in areas of Mars surface. The method illustrated in this work could be applied to hundreds of images to explore the chance to find potential methane macro-seepages.

Declarations

List of abbreviations:

Not applicable

Availability of data and materials:

The dataset analyzed in this work can be downloaded from <https://ode.rsl.wustl.edu/mars/>, the planetary simulator tool is available at this address <https://psg.gsfc.nasa.gov/>.

Competing interests:

The authors declare that they have no conflict of interest.

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Authors' contributions:

Paola Manzari: Conceptualization, Investigation, Elaboration of the code tool for hyperspectral data, Writing - review & editing.

Cosimo Marzo: Elaboration of the code tool for hyperspectral data, Conceptualization.

Eleonora Ammannito: Writing, Review, Editing.

All authors discussed the results and implications and commented on the manuscript at all stages.

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Figures

Figure 1

Areas selection. Colorized terrain base image from MOLA altimeter. Investigated areas: cyan asterisk= area of Oxia Planum; purple asterisk= area of Nili Fossae, yellow asterisk=area of Gale Crater.

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Figure 2

Example of investigated artefact. a) One band in grey scale of CRISM I/F observation frs0002a9b2, in Nili Fossae area. The image has the x axis corresponding to the width of the slit and the y axis that corresponds to the along track direction. Localization of the vertical artefact in the red frame. b) Mapping of 3.3 mm absorption; vertical artefact in the red frame. c) Spectrum of the corresponding pixel, showing the artefact in the 3.2-3.5 μm region.

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Figure 3

Cluster in frs0003a896. a) frs0003a896 image with a red cluster featured by spectral absorptions at 3.35; b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

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Cluster in frs0003a896. a) frs0003a896 image with a red cluster featured by spectral absorptions at 3.35; b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

Figure 4

Cluster in frs00028346. a) frs00028346 image with a red cluster featured by spectral absorptions at 3.35. b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

Figure 4

Cluster in frs00028346. a) frs00028346 image with a red cluster featured by spectral absorptions at 3.35. b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

Figure 5

Cluster in frs0002a9b2. a) frs0002a9b2 image with a red cluster featured by spectral absorptions at 3.3. b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

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Cluster in frs0002a9b2. a) frs0002a9b2 image with a red cluster featured by spectral absorptions at 3.3. b) zoom of the cluster. c) Corresponding absorption and fitting with MGM curve to extract spectral parameters.

Figure 6

PSG tool simulation. Simulated spectrum of frs0003a896 image, input parameters for the surface: 100% abundance Mars spectrum (PSG library) plus 100 ppbv of CH₄.

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Figure 7

Simulated transmittance spectra of frs0003a896 image, with increasing concentration of CH₄ from 40 ppbv to 500 ppbv.

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Simulated transmittance spectra of frs0003a896 image, with increasing concentration of CH₄ from 40 ppbv to 500 ppbv.

Figure 8

Simulations for Gale crater site. Quantification of the absorption depths for increasing concentration of CH₄ for the selected observations in Gale Crater area.

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Simulations for Gale crater site. Quantification of the absorption depths for increasing concentration of CH₄ for the selected observations in Gale Crater area.

Figure 9

Simulations for Oxia Planum site. Quantification of the absorption depths for increasing concentration of CH4 for the selected observations in Oxia Planum area.

Figure 9

Simulations for Oxia Planum site. Quantification of the absorption depths for increasing concentration of CH4 for the selected observations in Oxia Planum area.

Figure 10

Simulations for Nili Fossae site. Quantification of the absorption depths for increasing concentration of CH₄ for the selected observations in Nili Fossae area.

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Simulations for Nili Fossae site. Quantification of the absorption depths for increasing concentration of CH₄ for the selected observations in Nili Fossae area.

Figure 11

Schematic representation of the position of Mars respect to Sun (Season) during each considered CRISM observation.

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Schematic representation of the position of Mars respect to Sun (Season) during each considered CRISM observation.

Figure 12

Green: Radiance spectrum of featured pixels in the cluster of frs0002a9b2 image; Black: Corresponding I/F spectrum. The two spectra show that the absorption feature at 3.3 μm was present in radiance data and was not caused by the I/F calibration pipeline.

Figure 12

Green: Radiance spectrum of featured pixels in the cluster of frs0002a9b2 image; Black: Corresponding I/F spectrum. The two spectra show that the absorption feature at 3.3 μm was present in radiance data and was not caused by the I/F calibration pipeline.

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