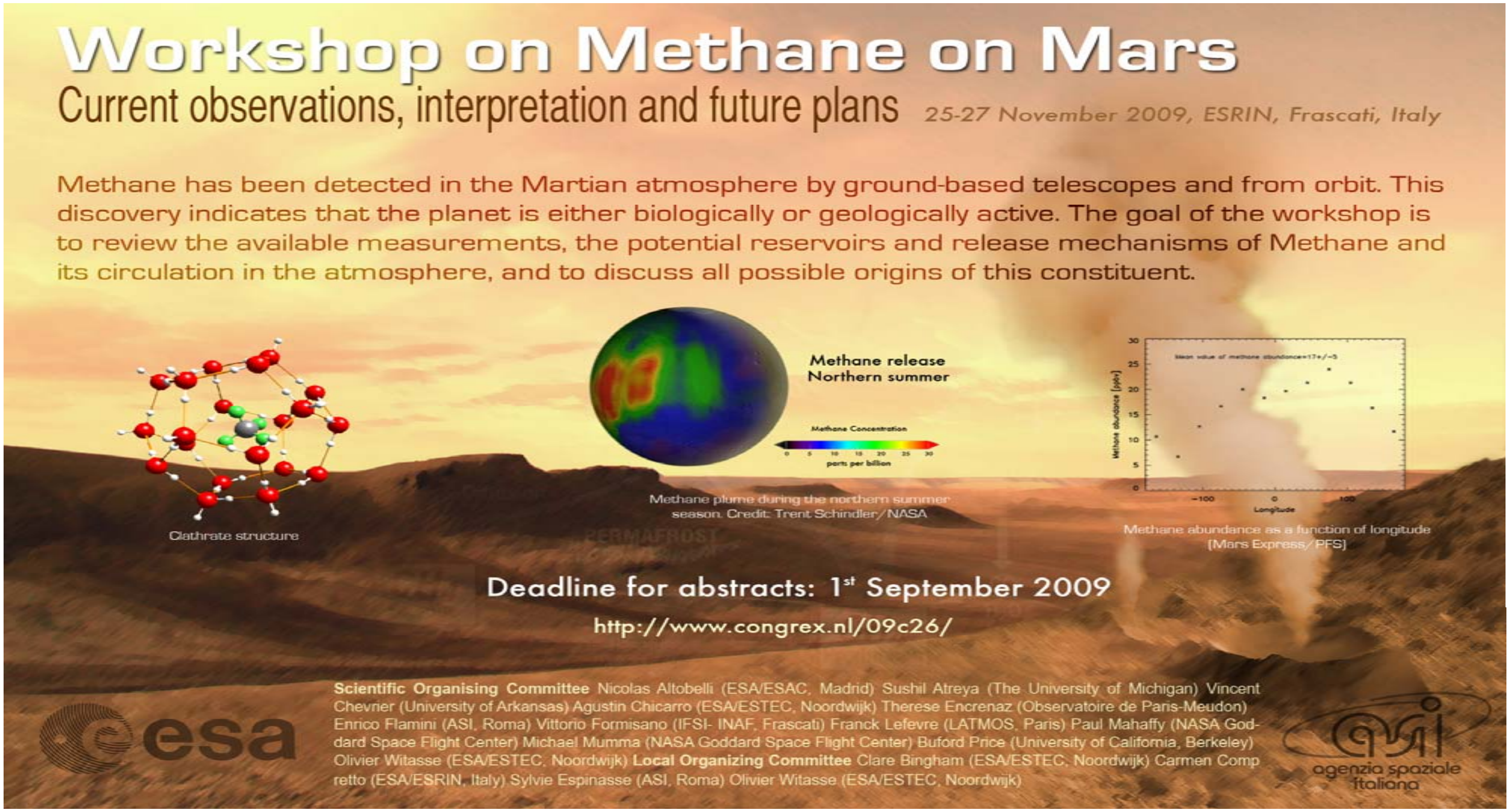
METHANE OBSERVATIONS
: AN HISTORICAL OVERVIEW

BY V.FORMISANO AND A. GEMINALE



Workshop on Methane on Mars

Current observations, interpretation and future plans 25-27 November 2009, ESRIN, Frascati, Italy

Methane has been detected in the Martian atmosphere by ground-based telescopes and from orbit. This discovery indicates that the planet is either biologically or geologically active. The goal of the workshop is to review the available measurements, the potential reservoirs and release mechanisms of Methane and its circulation in the atmosphere, and to discuss all possible origins of this constituent.

Clathrate structure

Methane release
Northern summer

Methane plume during the northern summer season. Credit: Trent Schindler/NASA

Methane abundance as a function of longitude
[Mars Express/PFS]

Deadline for abstracts: 1st September 2009

http://www.congrex.nl/09c26/

Scientific Organising Committee Nicolas Altobelli (ESA/ESAC, Madrid) Sushil Atreya (The University of Michigan) Vincent Chevrier (University of Arkansas) Agustin Chicarro (ESA/ESTEC, Noordwijk) Therese Encrenaz (Observatoire de Paris-Meudon) Enrico Flamini (ASI, Roma) Vittorio Formisano (IFSI- INAF, Frascati) Franck Lefevre (LATMOS, Paris) Paul Mahaffy (NASA Goddard Space Flight Center) Michael Mumma (NASA Goddard Space Flight Center) Buford Price (University of California, Berkeley) Olivier Witasse (ESA/ESTEC, Noordwijk) **Local Organizing Committee** Clare Bingham (ESA/ESTEC, Noordwijk) Carmen Compretto (ESA/ESRIN, Italy) Sylvie Espinasse (ASI, Roma) Olivier Witasse (ESA/ESTEC, Noordwijk)

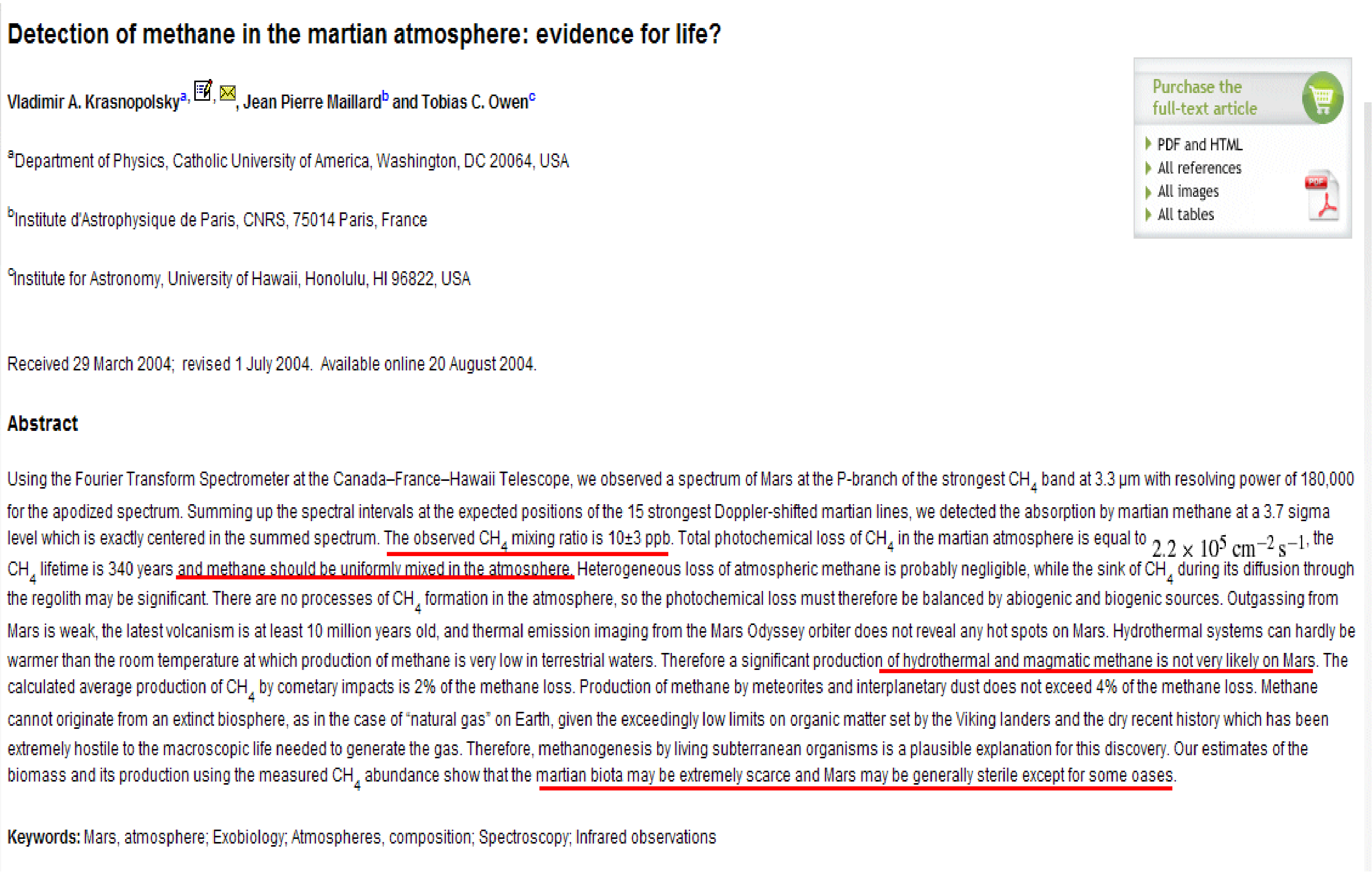
esa

asi agenzia spaziale italiana

2004

- 1- Three groups reported the observation of methane in Martian atmosphere: Krasnopolsky et al.(Icarus 2004) ,Formisano et al. (Science 2004), Mumma et al.DPS meeting(2004) .
- 2- Krasnopolsky reported one global measurement of 10 ppbv. No possibility of studying space or time variations.
- 3- Mumma reported 250 ppbv with space variations up to 600 ppbv or above.
- 4- Formisano reported an average value of 10 ppbv with space (and/or time?) variations from 0 to 35 ppbv. In particular it was reported a broad maximum in the longitudinal range of 50-170 E longitudes.

2004 Krasnopolsky



Detection of methane in the martian atmosphere: evidence for life?

Vladimir A. Krasnopolsky[a], , **Jean Pierre Maillard**[b] **and Tobias C. Owen**[c]

[a]Department of Physics, Catholic University of America, Washington, DC 20064, USA

[b]Institute d'Astrophysique de Paris, CNRS, 75014 Paris, France

[c]Institute for Astronomy, University of Hawaii, Honolulu, HI 96822, USA

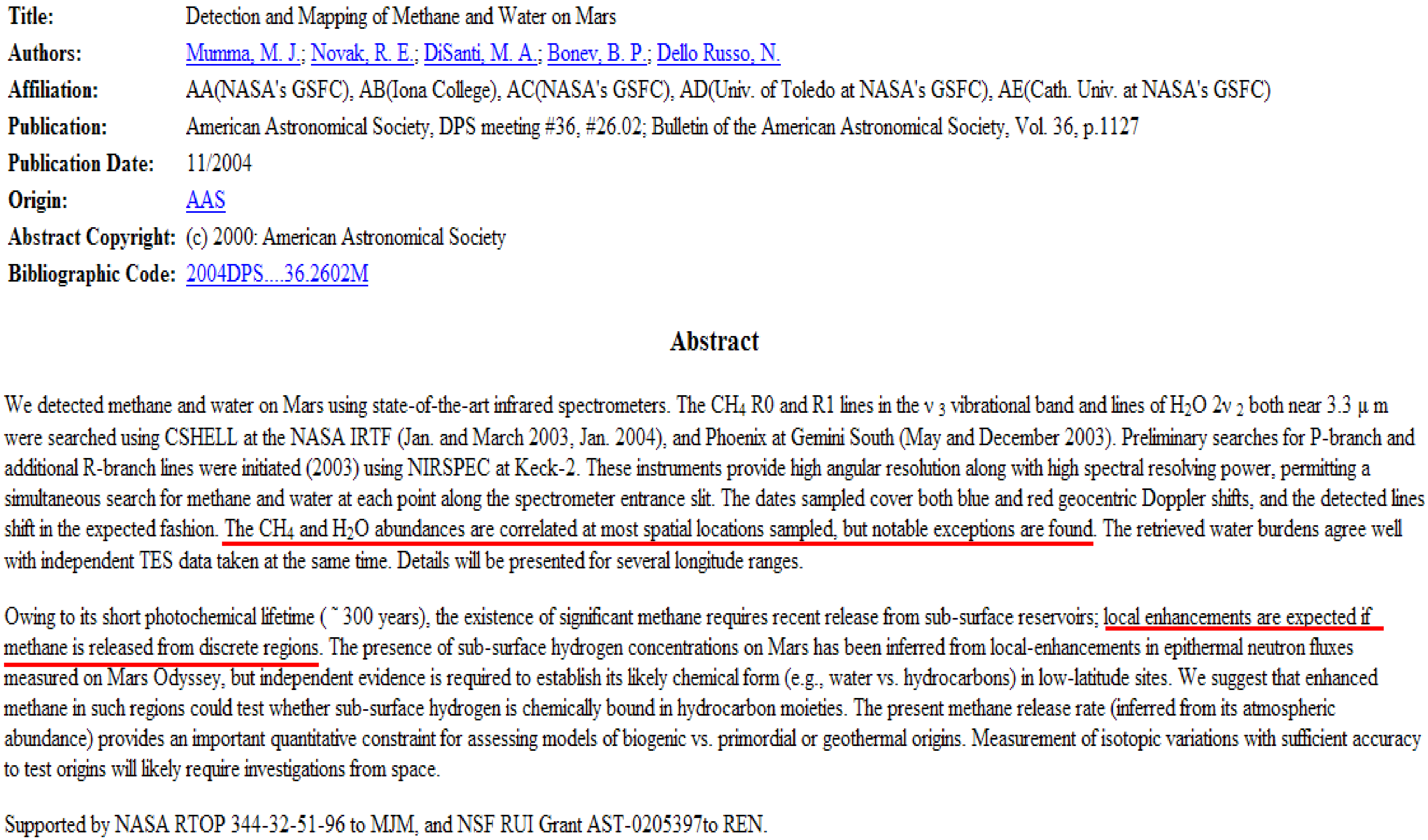
Received 29 March 2004; revised 1 July 2004. Available online 20 August 2004.

Abstract

Using the Fourier Transform Spectrometer at the Canada–France–Hawaii Telescope, we observed a spectrum of Mars at the P-branch of the strongest CH_4 band at 3.3 μm with resolving power of 180,000 for the apodized spectrum. Summing up the spectral intervals at the expected positions of the 15 strongest Doppler-shifted martian lines, we detected the absorption by martian methane at a 3.7 sigma level which is exactly centered in the summed spectrum. The observed CH_4 mixing ratio is 10±3 ppb. Total photochemical loss of CH_4 in the martian atmosphere is equal to $2.2\times10^5\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, the CH_4 lifetime is 340 years and methane should be uniformly mixed in the atmosphere. Heterogeneous loss of atmospheric methane is probably negligible, while the sink of CH_4 during its diffusion through the regolith may be significant. There are no processes of CH_4 formation in the atmosphere, so the photochemical loss must therefore be balanced by abiogenic and biogenic sources. Outgassing from Mars is weak, the latest volcanism is at least 10 million years old, and thermal emission imaging from the Mars Odyssey orbiter does not reveal any hot spots on Mars. Hydrothermal systems can hardly be warmer than the room temperature at which production of methane is very low in terrestrial waters. Therefore a significant production of hydrothermal and magmatic methane is not very likely on Mars. The calculated average production of CH_4 by cometary impacts is 2% of the methane loss. Production of methane by meteorites and interplanetary dust does not exceed 4% of the methane loss. Methane cannot originate from an extinct biosphere, as in the case of "natural gas" on Earth, given the exceedingly low limits on organic matter set by the Viking landers and the dry recent history which has been extremely hostile to the macroscopic life needed to generate the gas. Therefore, methanogenesis by living subterranean organisms is a plausible explanation for this discovery. Our estimates of the biomass and its production using the measured CH_4 abundance show that the martian biota may be extremely scarce and Mars may be generally sterile except for some oases.

Keywords: Mars, atmosphere; Exobiology; Atmospheres, composition; Spectroscopy; Infrared observations

Mumma 2004



Title:	Detection and Mapping of Methane and Water on Mars
Authors:	Mumma, M. J.; Novak, R. E.; DiSanti, M. A.; Bonev, B. P.; Dello Russo, N.
Affiliation:	AA(NASA's GSFC), AB(Iona College), AC(NASA's GSFC), AD(Univ. of Toledo at NASA's GSFC), AE(Cath. Univ. at NASA's GSFC)
Publication:	American Astronomical Society, DPS meeting #36, #26.02; Bulletin of the American Astronomical Society, Vol. 36, p.1127
Publication Date:	11/2004
Origin:	AAS
Abstract Copyright:	(c) 2000: American Astronomical Society
Bibliographic Code:	2004DPS....36.2602M

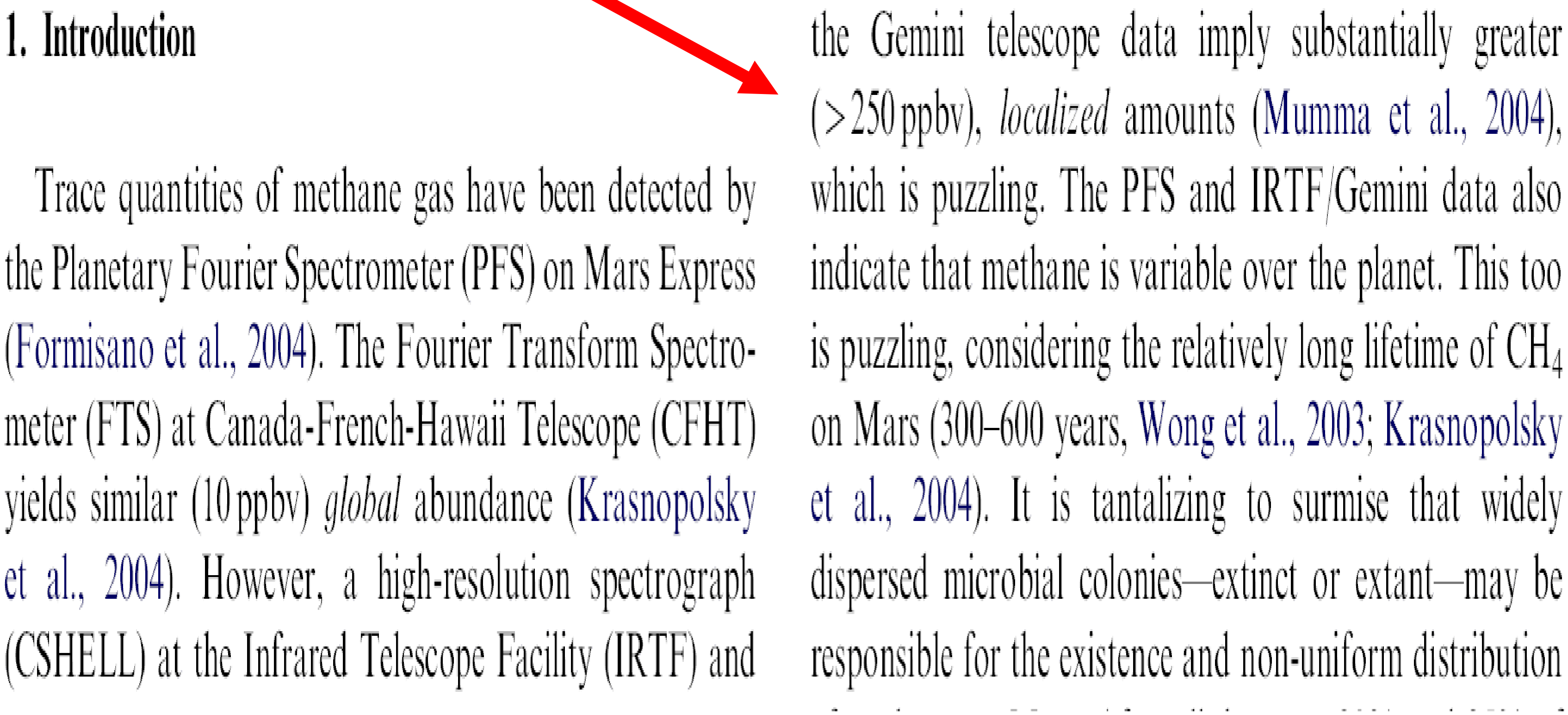
Abstract

We detected methane and water on Mars using state-of-the-art infrared spectrometers. The CH_4 R0 and R1 lines in the ν_3 vibrational band and lines of H_2O $2\nu_2$ both near 3.3 μ m were searched using CSHELL at the NASA IRTF (Jan. and March 2003, Jan. 2004), and Phoenix at Gemini South (May and December 2003). Preliminary searches for P-branch and additional R-branch lines were initiated (2003) using NIRSPEC at Keck-2. These instruments provide high angular resolution along with high spectral resolving power, permitting a simultaneous search for methane and water at each point along the spectrometer entrance slit. The dates sampled cover both blue and red geocentric Doppler shifts, and the detected lines shift in the expected fashion. The CH_4 and H_2O abundances are correlated at most spatial locations sampled, but notable exceptions are found. The retrieved water burdens agree well with independent TES data taken at the same time. Details will be presented for several longitude ranges.

Owing to its short photochemical lifetime (˜ 300 years), the existence of significant methane requires recent release from sub-surface reservoirs; local enhancements are expected if methane is released from discrete regions. The presence of sub-surface hydrogen concentrations on Mars has been inferred from local-enhancements in epithermal neutron fluxes measured on Mars Odyssey, but independent evidence is required to establish its likely chemical form (e.g., water vs. hydrocarbons) in low-latitude sites. We suggest that enhanced methane in such regions could test whether sub-surface hydrogen is chemically bound in hydrocarbon moieties. The present methane release rate (inferred from its atmospheric abundance) provides an important quantitative constraint for assessing models of biogenic vs. primordial or geothermal origins. Measurement of isotopic variations with sufficient accuracy to test origins will likely require investigations from space.

Supported by NASA RTOP 344-32-51-96 to MJM, and NSF RUI Grant AST-0205397to REN.

2004 Mumma (from Atreya)



1. Introduction

Trace quantities of methane gas have been detected by the Planetary Fourier Spectrometer (PFS) on Mars Express (Formisano et al., 2004). The Fourier Transform Spectrometer (FTS) at Canada-French-Hawaii Telescope (CFHT) yields similar (10 ppbv) *global* abundance (Krasnopolsky et al., 2004). However, a high-resolution spectrograph (CSHELL) at the Infrared Telescope Facility (IRTF) and the Gemini telescope data imply substantially greater (>250 ppbv), *localized* amounts (Mumma et al., 2004), which is puzzling. The PFS and IRTF/Gemini data also indicate that methane is variable over the planet. This too is puzzling, considering the relatively long lifetime of CH_4 on Mars (300–600 years, Wong et al., 2003; Krasnopolsky et al., 2004). It is tantalizing to surmise that widely dispersed microbial colonies—extinct or extant—may be responsible for the existence and non-uniform distribution

From Atreya et al . PSS,Vol 55,p.358 (2007)

2004 Formisano

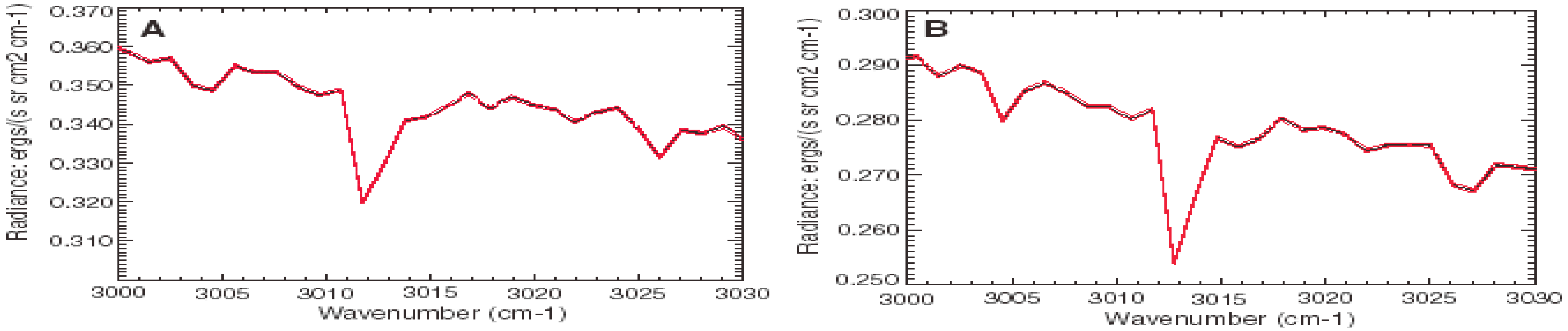


Fig. 1. (A) A portion of the first averaged PFS spectrum (January-February 2004, black curve), with $\pm 1\sigma$ confidence (red lines). The SNR is about 1300. Methane is identified at 3018 cm^{-1}. There are three water lines (at 3003.5, 3022, and 3026 cm^{-1}) and two solar lines (at 3012 and 3014 cm^{-1}). The continuum slope is due to water ice clouds in the atmosphere. The small peak at the left of the main solar line is due to instrumental response function. **(B)** The second averaged PFS spectrum (May 2004) in the same frequency interval. The caption is the same as for (A). The SNR is about 1500.

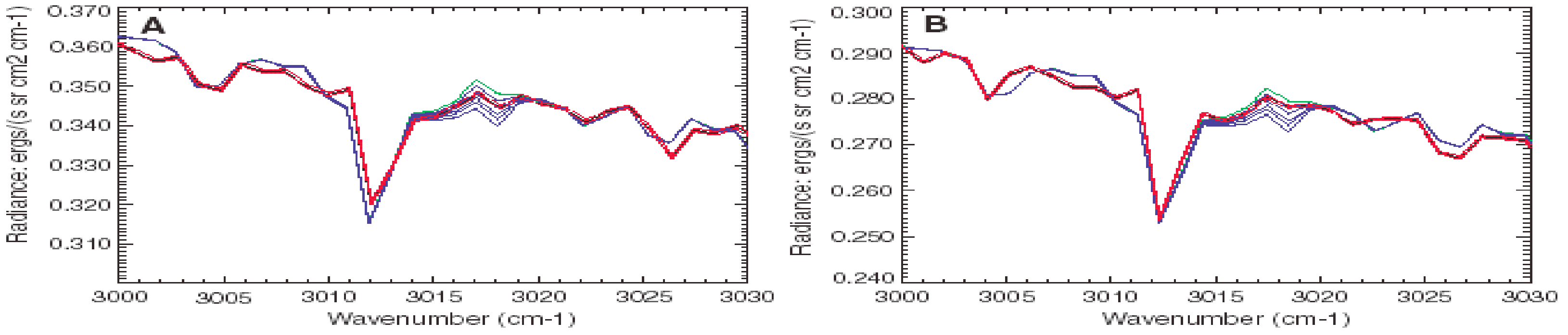


Fig. 2. (A) Synthetic spectra computed for 0 ppbv (green curve) and 10, 20, 30, 40, and 50 ppbv (violet curves) of methane, compared with the PFS average spectrum (black curve). The synthetic spectra have been computed for 6.7 millibars of CO_2, including 350 ppm of H_2O, along with dust and water ice clouds. The temperature profile obtained from simultaneous measurements in the thermal radiation was used. **(B)** Same as (A), with the PFS mean spectrum shown in Fig. 1B.

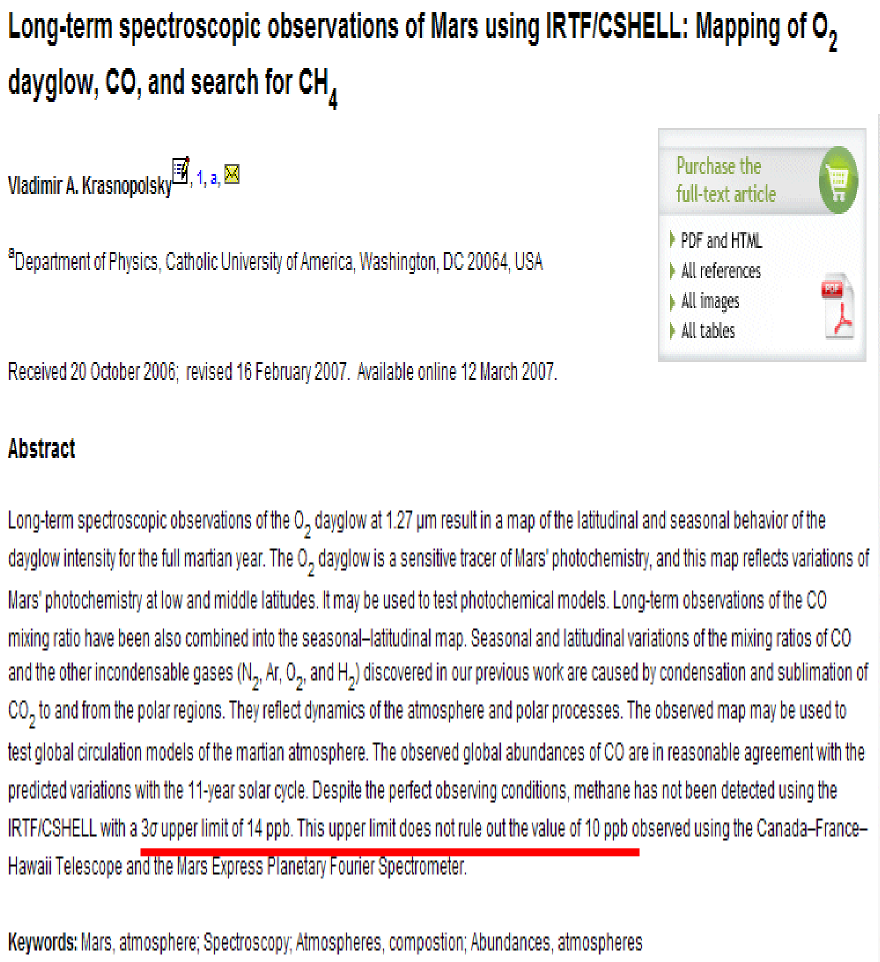
2004 Formisano

Fig. 5. Geographical distribution of the orbits considered: red (high methane mixing ratio), yellow (medium methane mixing ratio), and blue (low methane mixing ratio). Strong fluctuations occur in each of the three categories, indicating the possible presence of localized sources.

- Formisano et al 2004 attempt to map results: the red region (55° to 170° E) had 25 ppbv, the yellow region had 15 ppbv of methane on average, and the bleu region had less than 10 ppbv.
- Single orbit averages with either 0 or 35 ppbv were shown.

Mumma's methane enhancement region : Science 2009

2005-2009: Krasnopolsky



Long-term spectroscopic observations of Mars using IRTF/CSHELL: Mapping of O_2 dayglow, CO, and search for CH_4

Vladimir A. Krasnopolsky[1, a]

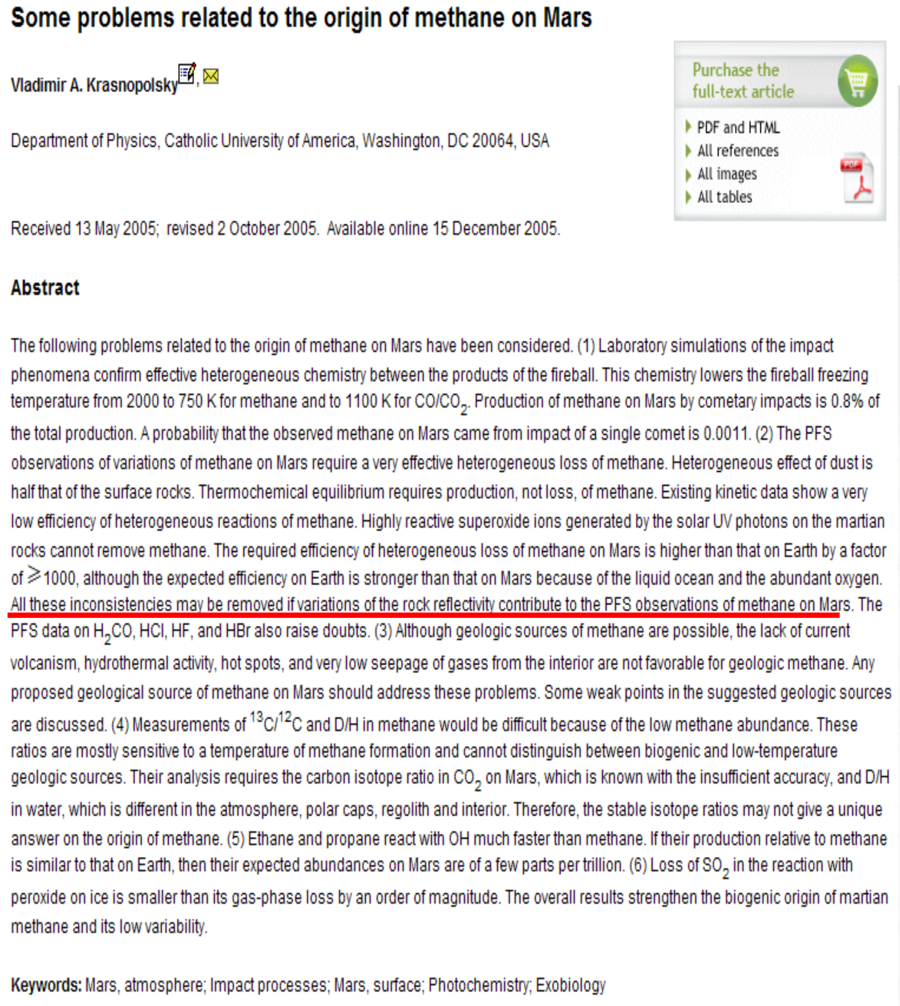
[a] Department of Physics, Catholic University of America, Washington, DC 20064, USA

Received 20 October 2006; revised 16 February 2007. Available online 12 March 2007.

Abstract

Long-term spectroscopic observations of the O_2 dayglow at 1.27 μm result in a map of the latitudinal and seasonal behavior of the dayglow intensity for the full martian year. The O_2 dayglow is a sensitive tracer of Mars' photochemistry, and this map reflects variations of Mars' photochemistry at low and middle latitudes. It may be used to test photochemical models. Long-term observations of the CO mixing ratio have been also combined into the seasonal–latitudinal map. Seasonal and latitudinal variations of the mixing ratios of CO and the other incondensable gases (N_2, Ar, O_2, and H_2) discovered in our previous work are caused by condensation and sublimation of CO_2 to and from the polar regions. They reflect dynamics of the atmosphere and polar processes. The observed map may be used to test global circulation models of the martian atmosphere. The observed global abundances of CO are in reasonable agreement with the predicted variations with the 11-year solar cycle. Despite the perfect observing conditions, methane has not been detected using the IRTF/CSHELL with a 3σ upper limit of 14 ppb. This upper limit does not rule out the value of 10 ppb observed using the Canada–France–Hawaii Telescope and the Mars Express Planetary Fourier Spectrometer.

Keywords: Mars, atmosphere; Spectroscopy; Atmospheres, compostion; Abundances, atmospheres



Some problems related to the origin of methane on Mars

Vladimir A. Krasnopolsky

Department of Physics, Catholic University of America, Washington, DC 20064, USA

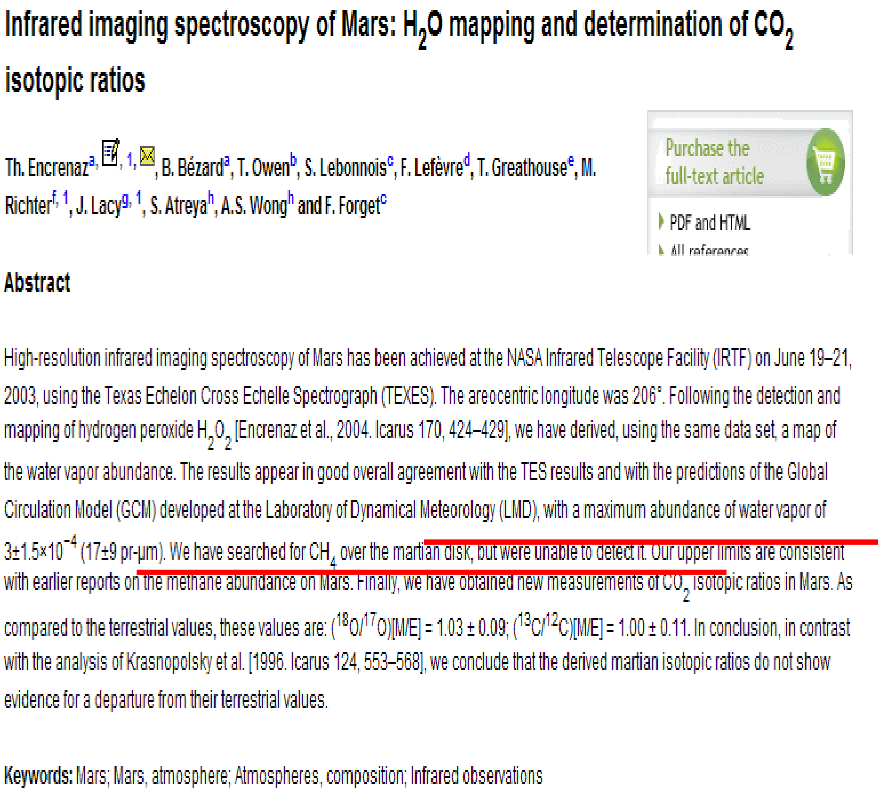
Received 13 May 2005; revised 2 October 2005. Available online 15 December 2005.

Abstract

The following problems related to the origin of methane on Mars have been considered. (1) Laboratory simulations of the impact phenomena confirm effective heterogeneous chemistry between the products of the fireball. This chemistry lowers the fireball freezing temperature from 2000 to 750 K for methane and to 1100 K for CO/CO_2. Production of methane on Mars by cometary impacts is 0.8% of the total production. A probability that the observed methane on Mars came from impact of a single comet is 0.0011. (2) The PFS observations of variations of methane on Mars require a very effective heterogeneous loss of methane. Heterogeneous effect of dust is half that of the surface rocks. Thermochemical equilibrium requires production, not loss, of methane. Existing kinetic data show a very low efficiency of heterogeneous reactions of methane. Highly reactive superoxide ions generated by the solar UV photons on the martian rocks cannot remove methane. The required efficiency of heterogeneous loss of methane on Mars is higher than that on Earth by a factor of $\geqslant 1000$, although the expected efficiency on Earth is stronger than that on Mars because of the liquid ocean and the abundant oxygen. All these inconsistencies may be removed if variations of the rock reflectivity contribute to the PFS observations of methane on Mars. The PFS data on H_2CO, HCl, HF, and HBr also raise doubts. (3) Although geologic sources of methane are possible, the lack of current volcanism, hydrothermal activity, hot spots, and very low seepage of gases from the interior are not favorable for geologic methane. Any proposed geological source of methane on Mars should address these problems. Some weak points in the suggested geologic sources are discussed. (4) Measurements of $^{13}C/^{12}C$ and D/H in methane would be difficult because of the low methane abundance. These ratios are mostly sensitive to a temperature of methane formation and cannot distinguish between biogenic and low-temperature geologic sources. Their analysis requires the carbon isotope ratio in CO_2 on Mars, which is known with the insufficient accuracy, and D/H in water, which is different in the atmosphere, polar caps, regolith and interior. Therefore, the stable isotope ratios may not give a unique answer on the origin of methane. (5) Ethane and propane react with OH much faster than methane. If their production relative to methane is similar to that on Earth, then their expected abundances on Mars are of a few parts per trillion. (6) Loss of SO_2 in the reaction with peroxide on ice is smaller than its gas-phase loss by an order of magnitude. The overall results strengthen the biogenic origin of martian methane and its low variability.

Keywords: Mars, atmosphere; Impact processes; Mars, surface; Photochemistry; Exobiology

2005-2009: Encrenaz



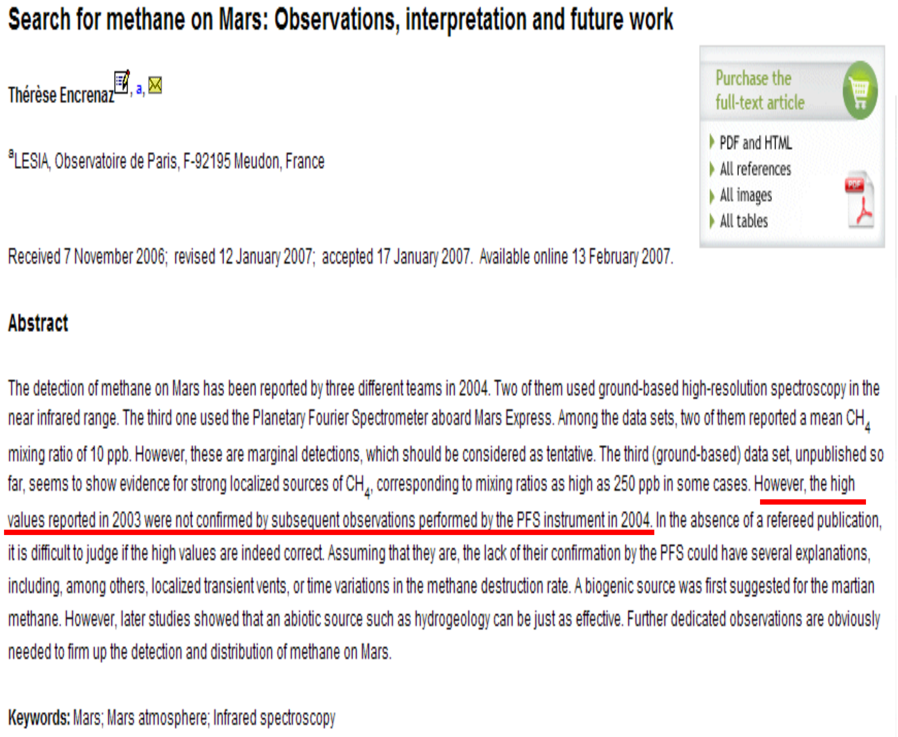
Infrared imaging spectroscopy of Mars: H_2O mapping and determination of CO_2 isotopic ratios

Th. Encrenaz[a, 1], B. Bézard[a], T. Owen[b], S. Lebonnois[c], F. Lefèvre[d], T. Greathouse[e], M. Richter[f, 1], J. Lacy[g, 1], S. Atreya[h], A.S. Wong[h] and F. Forget[c]

Abstract

High-resolution infrared imaging spectroscopy of Mars has been achieved at the NASA Infrared Telescope Facility (IRTF) on June 19–21, 2003, using the Texas Echelon Cross Echelle Spectrograph (TEXES). The areocentric longitude was 206°. Following the detection and mapping of hydrogen peroxide H_2O_2 [Encrenaz et al., 2004. Icarus 170, 424–429], we have derived, using the same data set, a map of the water vapor abundance. The results appear in good overall agreement with the TES results and with the predictions of the Global Circulation Model (GCM) developed at the Laboratory of Dynamical Meteorology (LMD), with a maximum abundance of water vapor of $3\pm1.5\times10^{-4}$ (17±9 pr-μm). We have searched for CH_4 over the martian disk, but were unable to detect it. Our upper limits are consistent with earlier reports on the methane abundance on Mars. Finally, we have obtained new measurements of CO_2 isotopic ratios in Mars. As compared to the terrestrial values, these values are: $(^{18}O/^{17}O)[M/E] = 1.03 \pm 0.09$; $(^{13}C/^{12}C)[M/E] = 1.00 \pm 0.11$. In conclusion, in contrast with the analysis of Krasnopolsky et al. [1996. Icarus 124, 553–568], we conclude that the derived martian isotopic ratios do not show evidence for a departure from their terrestrial values.

Keywords: Mars; Mars, atmosphere; Atmospheres, composition; Infrared observations



Search for methane on Mars: Observations, interpretation and future work

Thérèse Encrenaz[a]

[a]LESIA, Observatoire de Paris, F-92195 Meudon, France

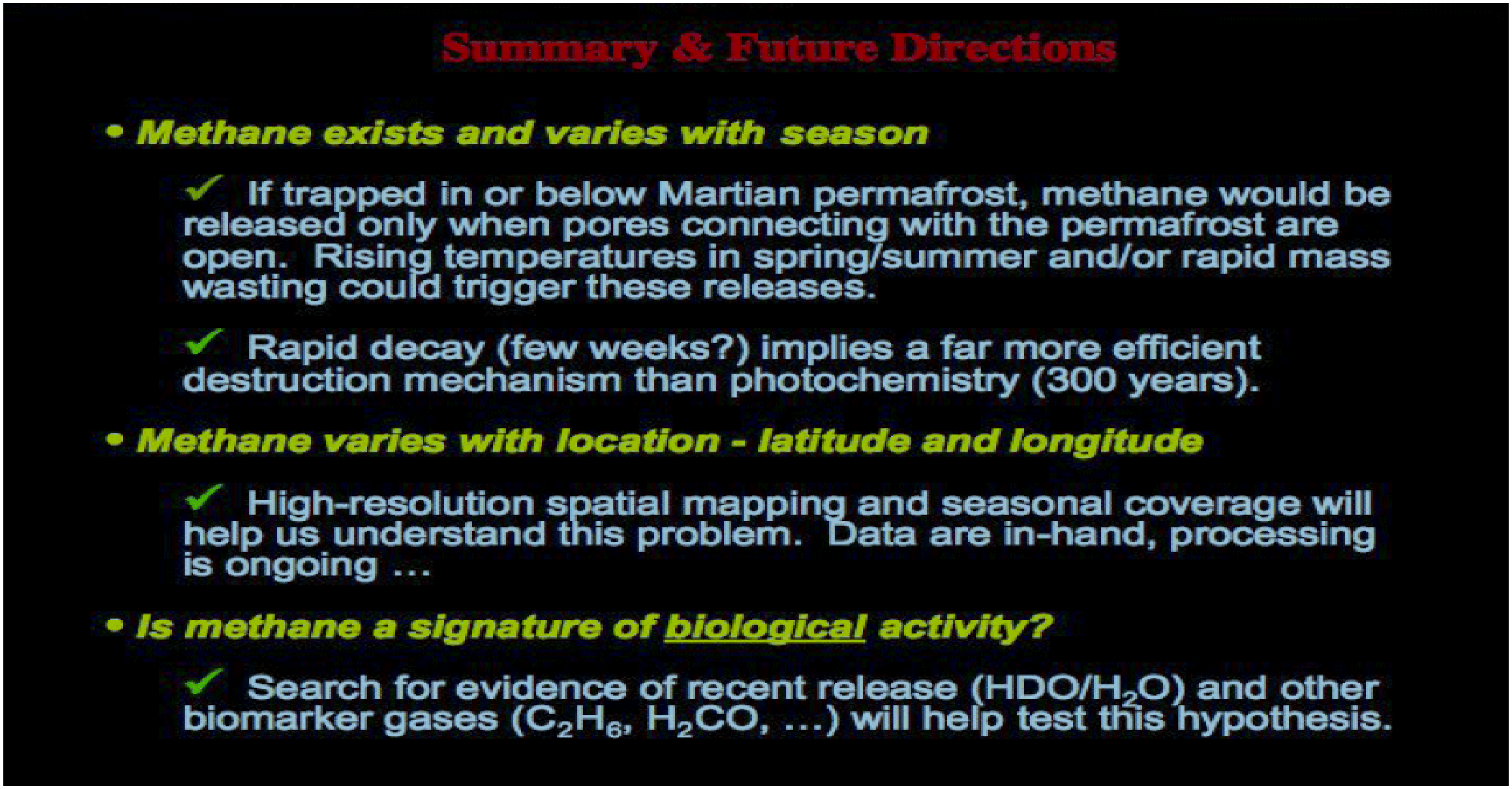
Received 7 November 2006; revised 12 January 2007; accepted 17 January 2007. Available online 13 February 2007.

Abstract

The detection of methane on Mars has been reported by three different teams in 2004. Two of them used ground-based high-resolution spectroscopy in the near infrared range. The third one used the Planetary Fourier Spectrometer aboard Mars Express. Among the data sets, two of them reported a mean CH_4 mixing ratio of 10 ppb. However, these are marginal detections, which should be considered as tentative. The third (ground-based) data set, unpublished so far, seems to show evidence for strong localized sources of CH_4, corresponding to mixing ratios as high as 250 ppb in some cases. However, the high values reported in 2003 were not confirmed by subsequent observations performed by the PFS instrument in 2004. In the absence of a refereed publication, it is difficult to judge if the high values are indeed correct. Assuming that they are, the lack of their confirmation by the PFS could have several explanations, including, among others, localized transient vents, or time variations in the methane destruction rate. A biogenic source was first suggested for the martian methane. However, later studies showed that an abiotic source such as hydrogeology can be just as effective. Further dedicated observations are obviously needed to firm up the detection and distribution of methane on Mars.

Keywords: Mars; Mars atmosphere; Infrared spectroscopy

2005-2009: Mumma 2007

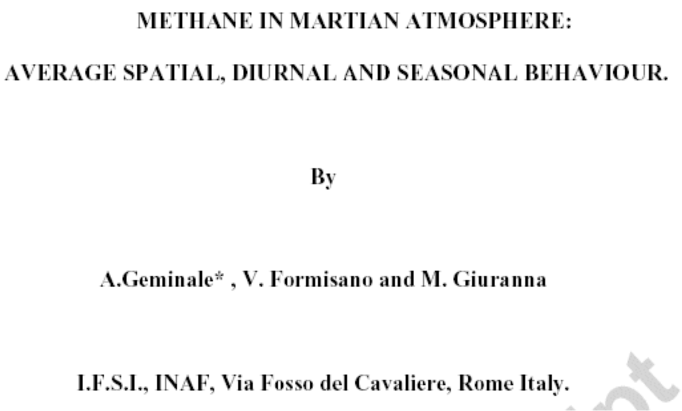


Summary & Future Directions

- ***Methane exists and varies with season***
  - ✓ If trapped in or below Martian permafrost, methane would be released only when pores connecting with the permafrost are open. Rising temperatures in spring/summer and/or rapid mass wasting could trigger these releases.
  - ✓ Rapid decay (few weeks?) implies a far more efficient destruction mechanism than photochemistry (300 years).
- ***Methane varies with location - latitude and longitude***
  - ✓ High-resolution spatial mapping and seasonal coverage will help us understand this problem. Data are in-hand, processing is ongoing …
- ***Is methane a signature of biological activity?***
  - ✓ Search for evidence of recent release (HDO/H_2O) and other biomarker gases (C_2H_6, H_2CO, …) will help test this hypothesis.

Methane mixing ratio was reported to be between 0 and 50 ppbv.

2005-2009: PFS-MEX

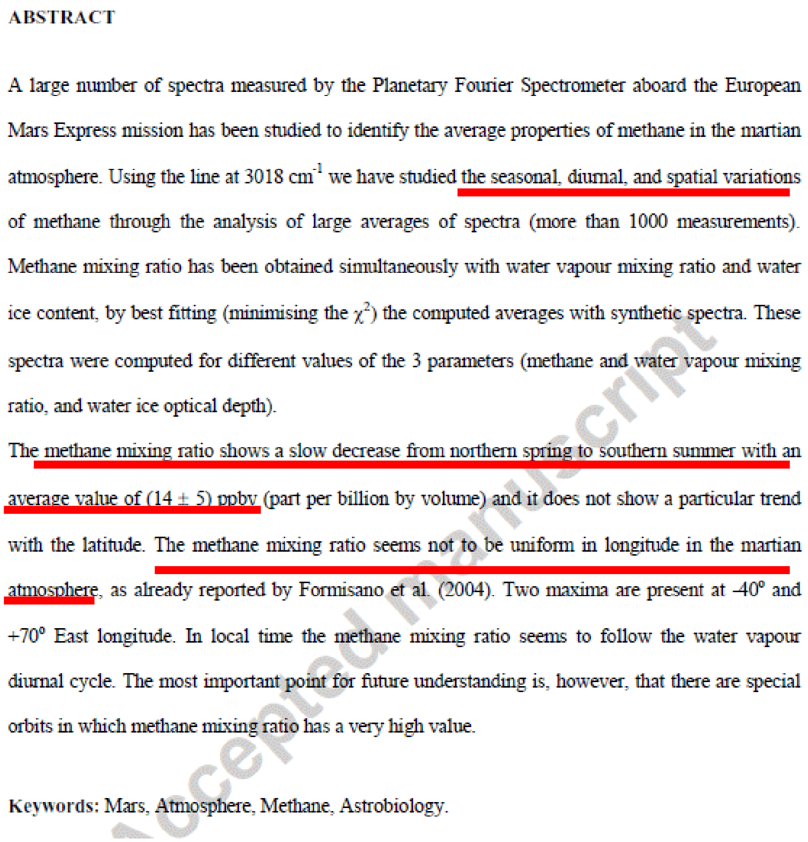


METHANE IN MARTIAN ATMOSPHERE:
AVERAGE SPATIAL, DIURNAL AND SEASONAL BEHAVIOUR.

By

A.Geminale* , V. Formisano and M. Giuranna

I.F.S.I., INAF, Via Fosso del Cavaliere, Rome Italy.



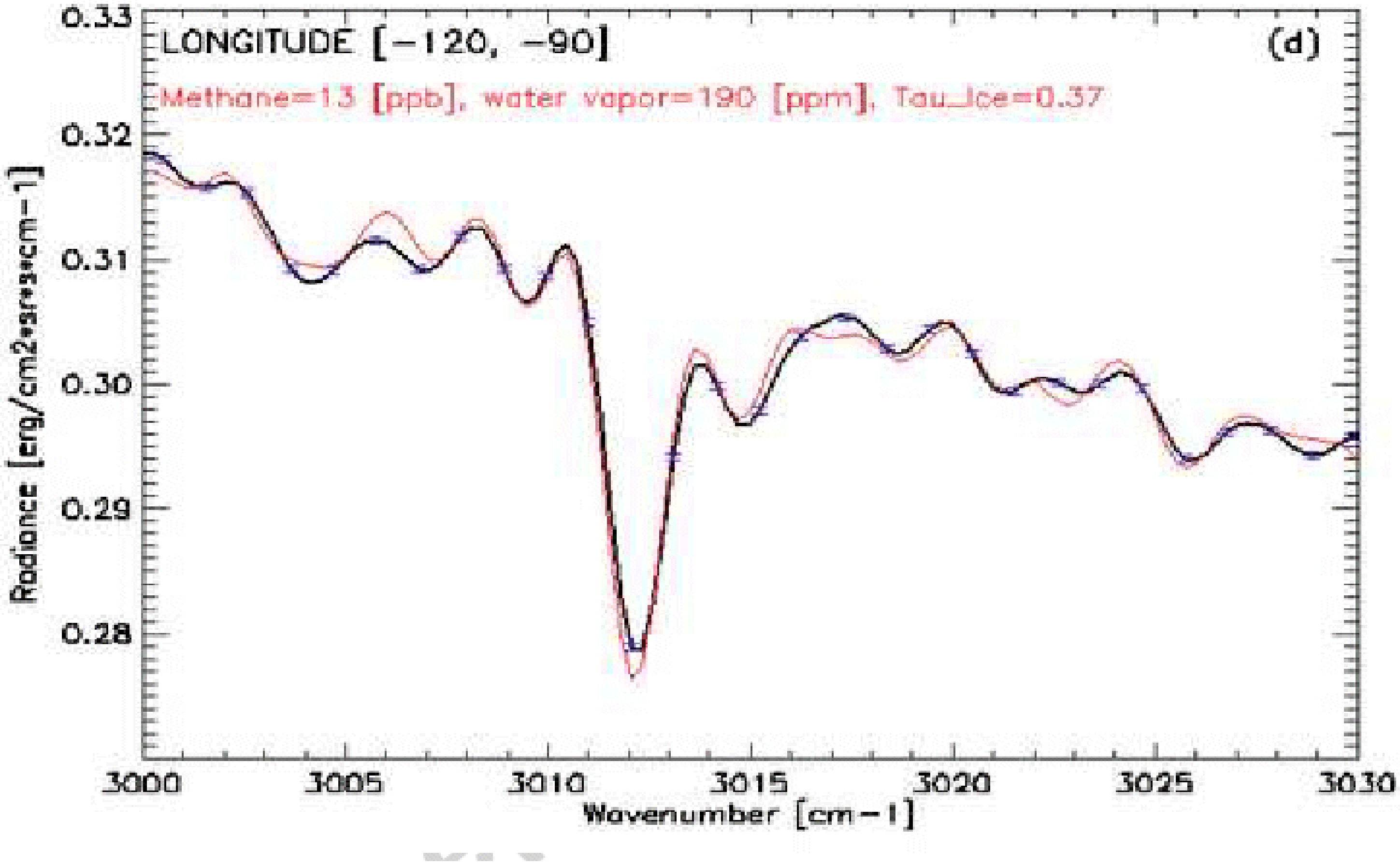
ABSTRACT

A large number of spectra measured by the Planetary Fourier Spectrometer aboard the European Mars Express mission has been studied to identify the average properties of methane in the martian atmosphere. Using the line at 3018 cm^{-1} we have studied the seasonal, diurnal, and spatial variations of methane through the analysis of large averages of spectra (more than 1000 measurements). Methane mixing ratio has been obtained simultaneously with water vapour mixing ratio and water ice content, by best fitting (minimising the χ^2) the computed averages with synthetic spectra. These spectra were computed for different values of the 3 parameters (methane and water vapour mixing ratio, and water ice optical depth).

The methane mixing ratio shows a slow decrease from northern spring to southern summer with an average value of (14 ± 5) ppbv (part per billion by volume) and it does not show a particular trend with the latitude. The methane mixing ratio seems not to be uniform in longitude in the martian atmosphere, as already reported by Formisano et al. (2004). Two maxima are present at -40° and +70° East longitude. In local time the methane mixing ratio seems to follow the water vapour diurnal cycle. The most important point for future understanding is, however, that there are special orbits in which methane mixing ratio has a very high value.

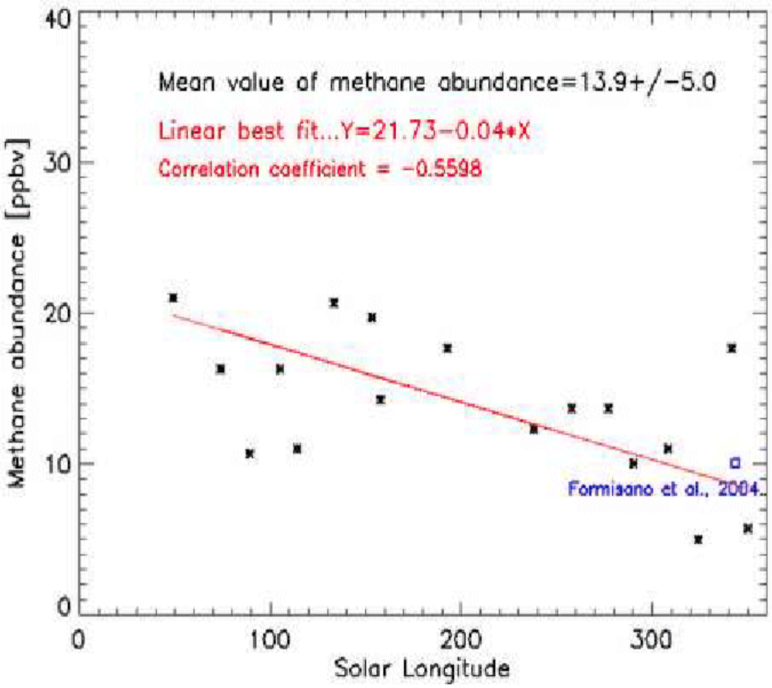
Keywords: Mars, Atmosphere, Methane, Astrobiology.

2005-2009: PFS-MEX

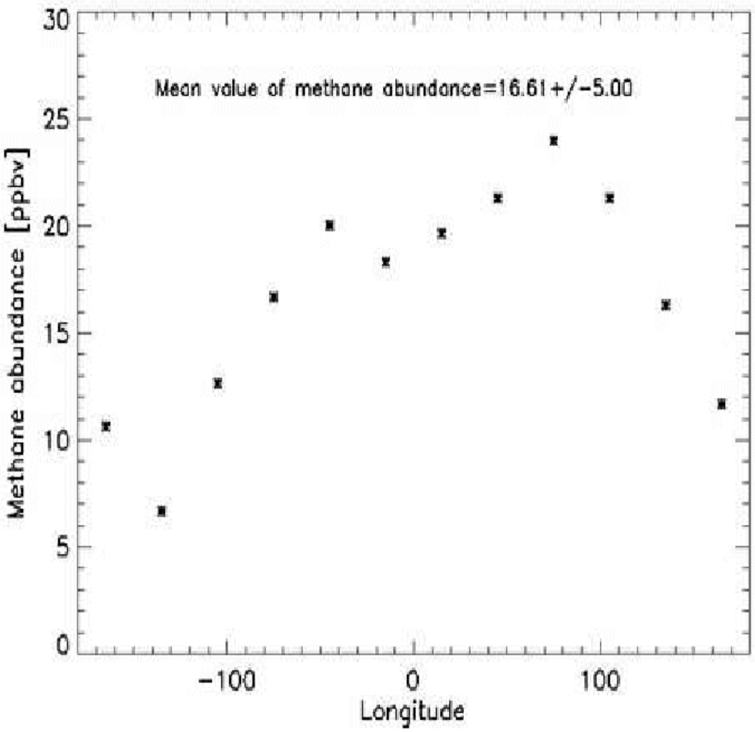


New approach to the data: add zeroes to interferogram to better evaluate location and intensity of lines.

2005-2009: PFS-MEX

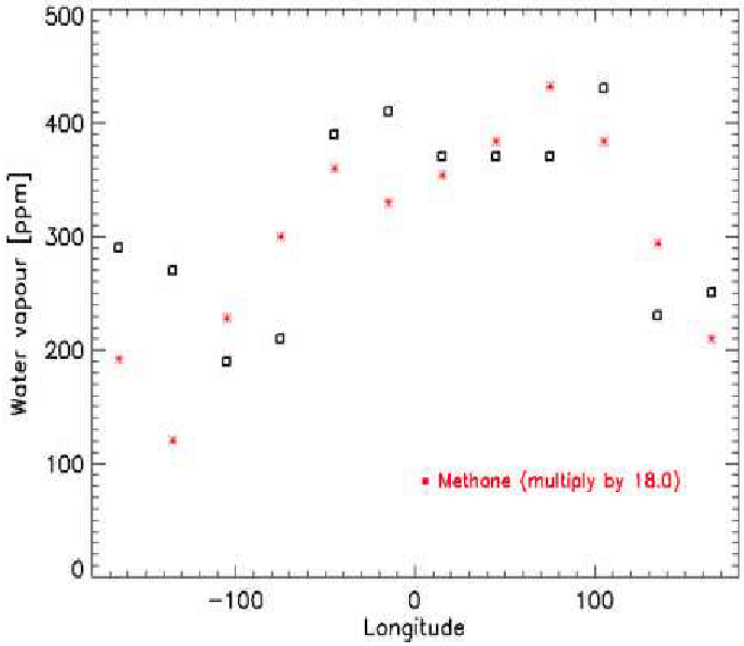


Seasonal behaviour of methane mixing ratio

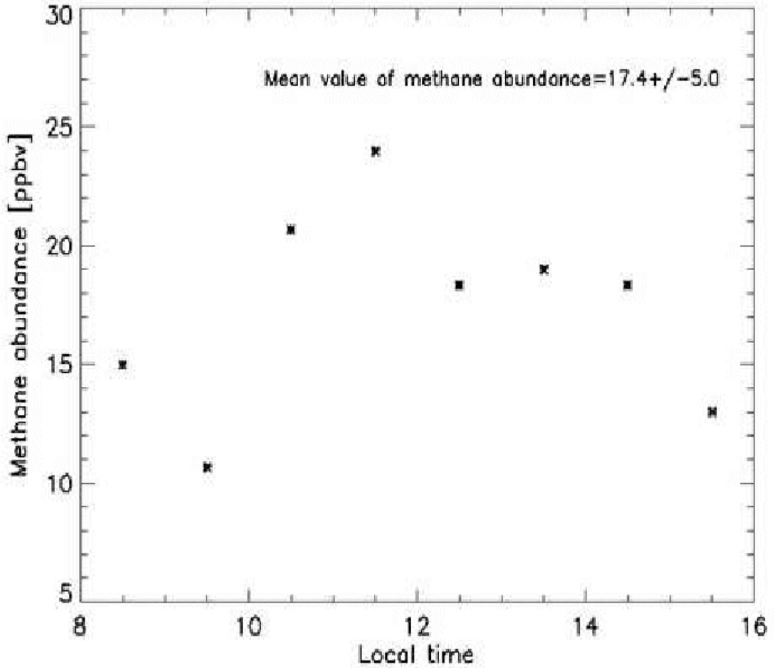


Longitude behaviour of methane: a maximum at 75 deg E longitude

2005-2009: PFS-MEX

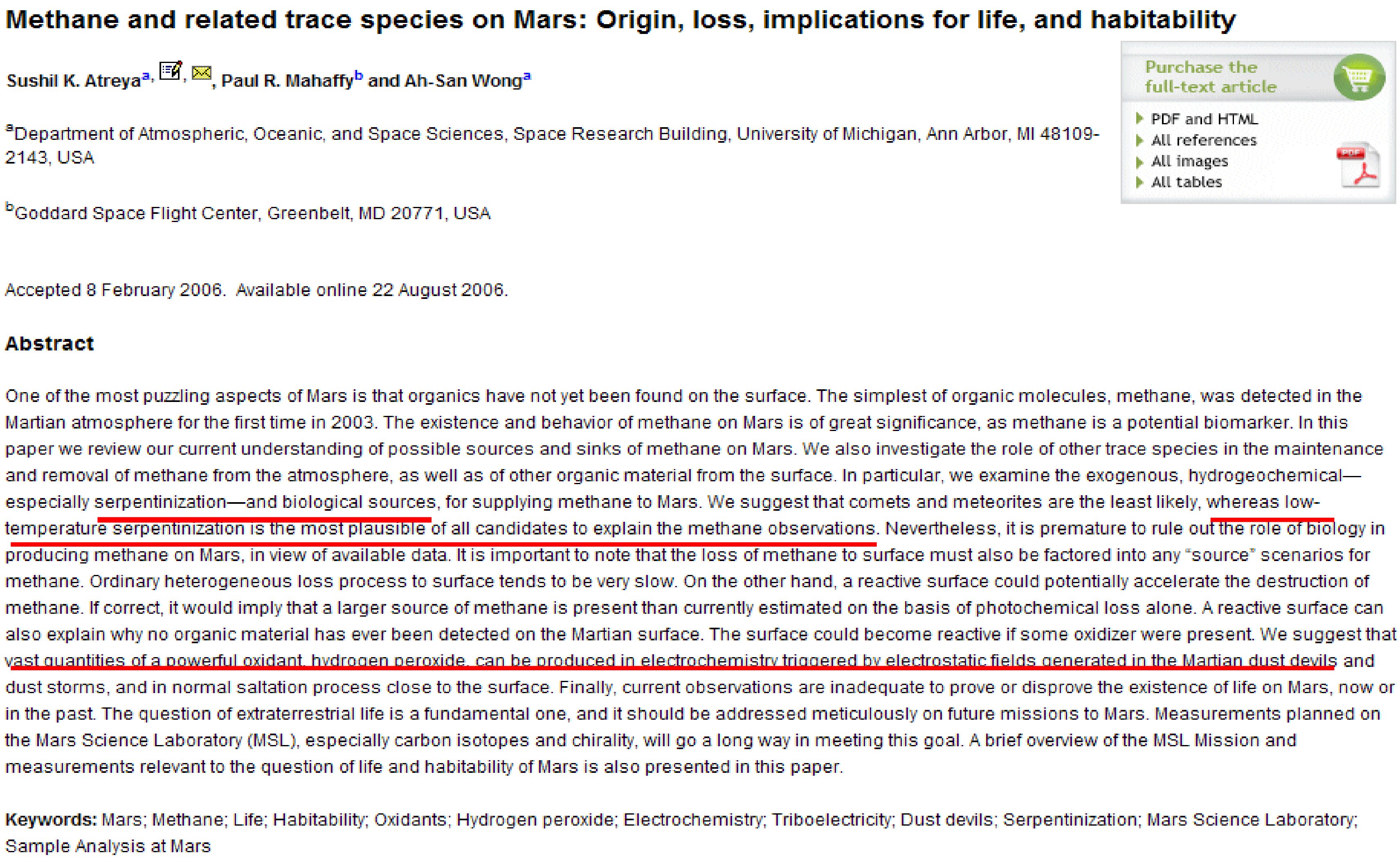


“correlation” between methane and water vapor: not a real correlation , but pointing to the same source.



Methane behaviour with local time

2005-2009 : Atreya



Methane and related trace species on Mars: Origin, loss, implications for life, and habitability

Sushil K. Atreya[a], **Paul R. Mahaffy**[b] **and Ah-San Wong**[a]

[a]Department of Atmospheric, Oceanic, and Space Sciences, Space Research Building, University of Michigan, Ann Arbor, MI 48109-2143, USA

[b]Goddard Space Flight Center, Greenbelt, MD 20771, USA

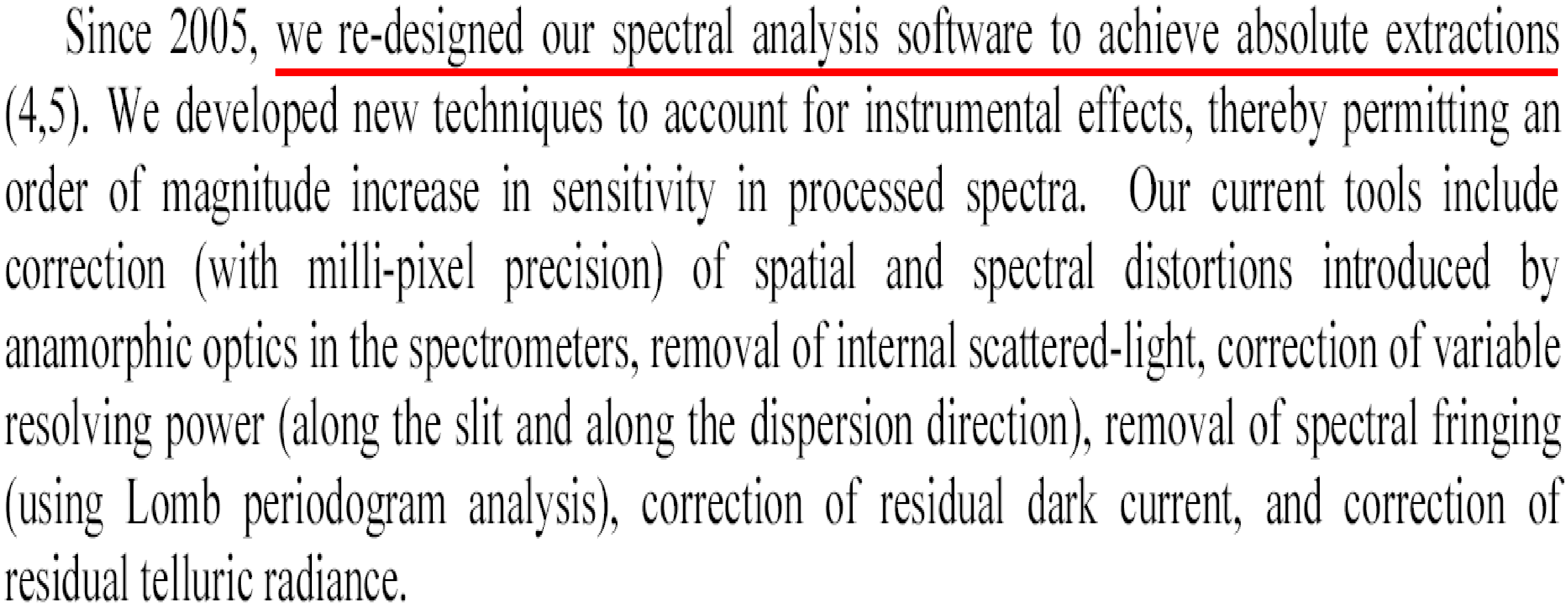
Accepted 8 February 2006. Available online 22 August 2006.

Abstract

One of the most puzzling aspects of Mars is that organics have not yet been found on the surface. The simplest of organic molecules, methane, was detected in the Martian atmosphere for the first time in 2003. The existence and behavior of methane on Mars is of great significance, as methane is a potential biomarker. In this paper we review our current understanding of possible sources and sinks of methane on Mars. We also investigate the role of other trace species in the maintenance and removal of methane from the atmosphere, as well as of other organic material from the surface. In particular, we examine the exogenous, hydrogeochemical—especially serpentinization—and biological sources, for supplying methane to Mars. We suggest that comets and meteorites are the least likely, whereas low-temperature serpentinization is the most plausible of all candidates to explain the methane observations. Nevertheless, it is premature to rule out the role of biology in producing methane on Mars, in view of available data. It is important to note that the loss of methane to surface must also be factored into any "source" scenarios for methane. Ordinary heterogeneous loss process to surface tends to be very slow. On the other hand, a reactive surface could potentially accelerate the destruction of methane. If correct, it would imply that a larger source of methane is present than currently estimated on the basis of photochemical loss alone. A reactive surface can also explain why no organic material has ever been detected on the Martian surface. The surface could become reactive if some oxidizer were present. We suggest that vast quantities of a powerful oxidant, hydrogen peroxide, can be produced in electrochemistry triggered by electrostatic fields generated in the Martian dust devils and dust storms, and in normal saltation process close to the surface. Finally, current observations are inadequate to prove or disprove the existence of life on Mars, now or in the past. The question of extraterrestrial life is a fundamental one, and it should be addressed meticulously on future missions to Mars. Measurements planned on the Mars Science Laboratory (MSL), especially carbon isotopes and chirality, will go a long way in meeting this goal. A brief overview of the MSL Mission and measurements relevant to the question of life and habitability of Mars is also presented in this paper.

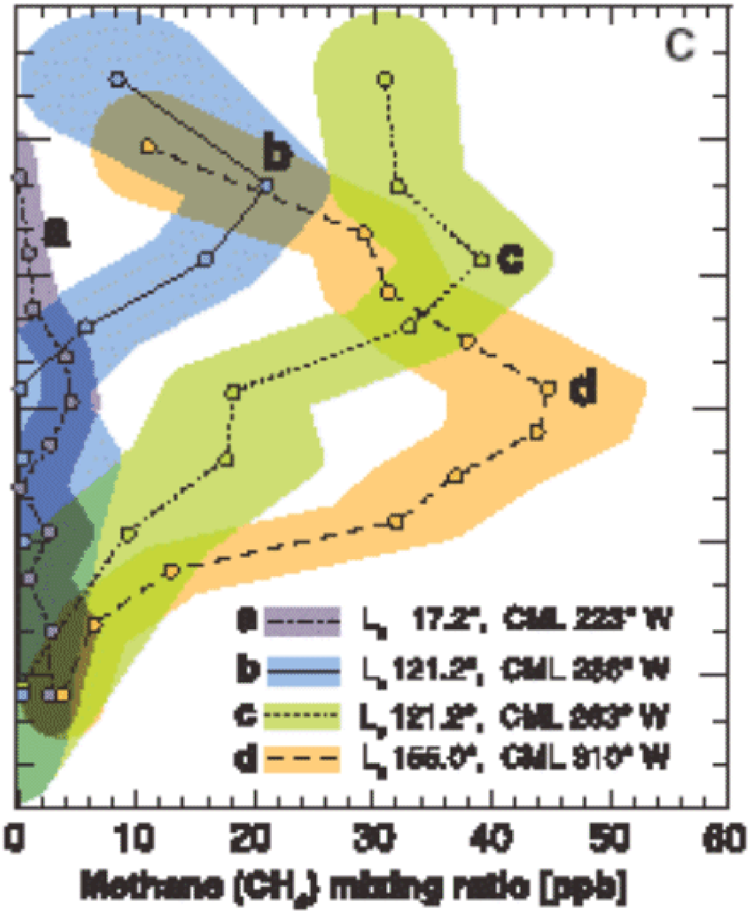
Keywords: Mars; Methane; Life; Habitability; Oxidants; Hydrogen peroxide; Electrochemistry; Triboelectricity; Dust devils; Serpentinization; Mars Science Laboratory; Sample Analysis at Mars

Recent: Mumma Science



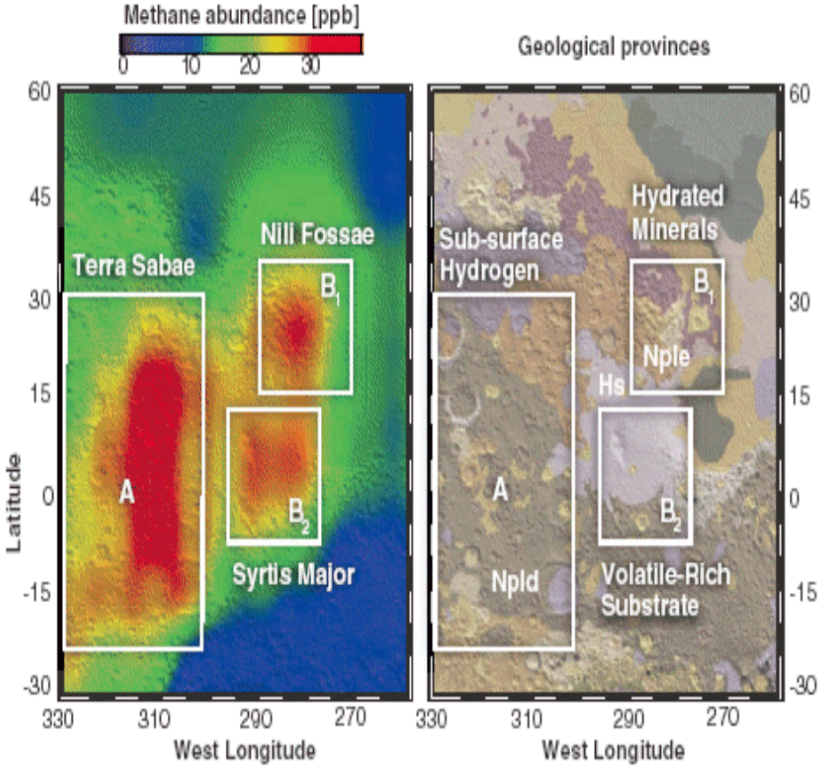
Since 2005, we re-designed our spectral analysis software to achieve absolute extractions (4,5). We developed new techniques to account for instrumental effects, thereby permitting an order of magnitude increase in sensitivity in processed spectra. Our current tools include correction (with milli-pixel precision) of spatial and spectral distortions introduced by anamorphic optics in the spectrometers, removal of internal scattered-light, correction of variable resolving power (along the slit and along the dispersion direction), removal of spectral fringing (using Lomb periodogram analysis), correction of residual dark current, and correction of residual telluric radiance.

2005-2009: Mumma



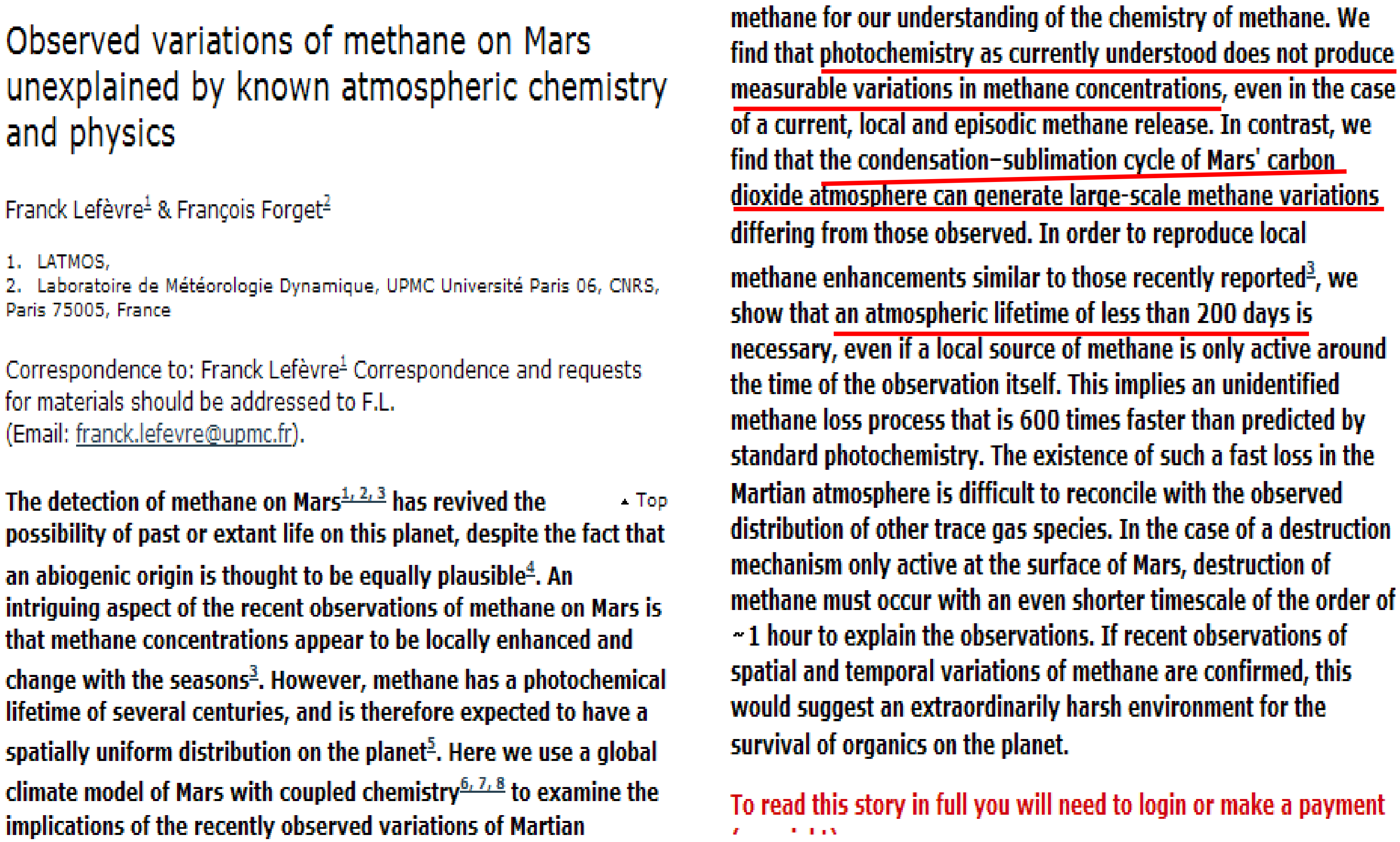
- After the revision of the data analysis, the resulting mixing ratios of Mumma et al. Coincide rather well with the results of PFS : methane mixing is between 0 and 45-50 ppbv

2005-2009: Mumma



- The methane plume observed by Mumma in 270- 330 W longitude (= 30-90 E longitude) corresponds to the methane enhancement found by PFS at 50-170 E longitude.

Recent Lefevre-Forget



Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics

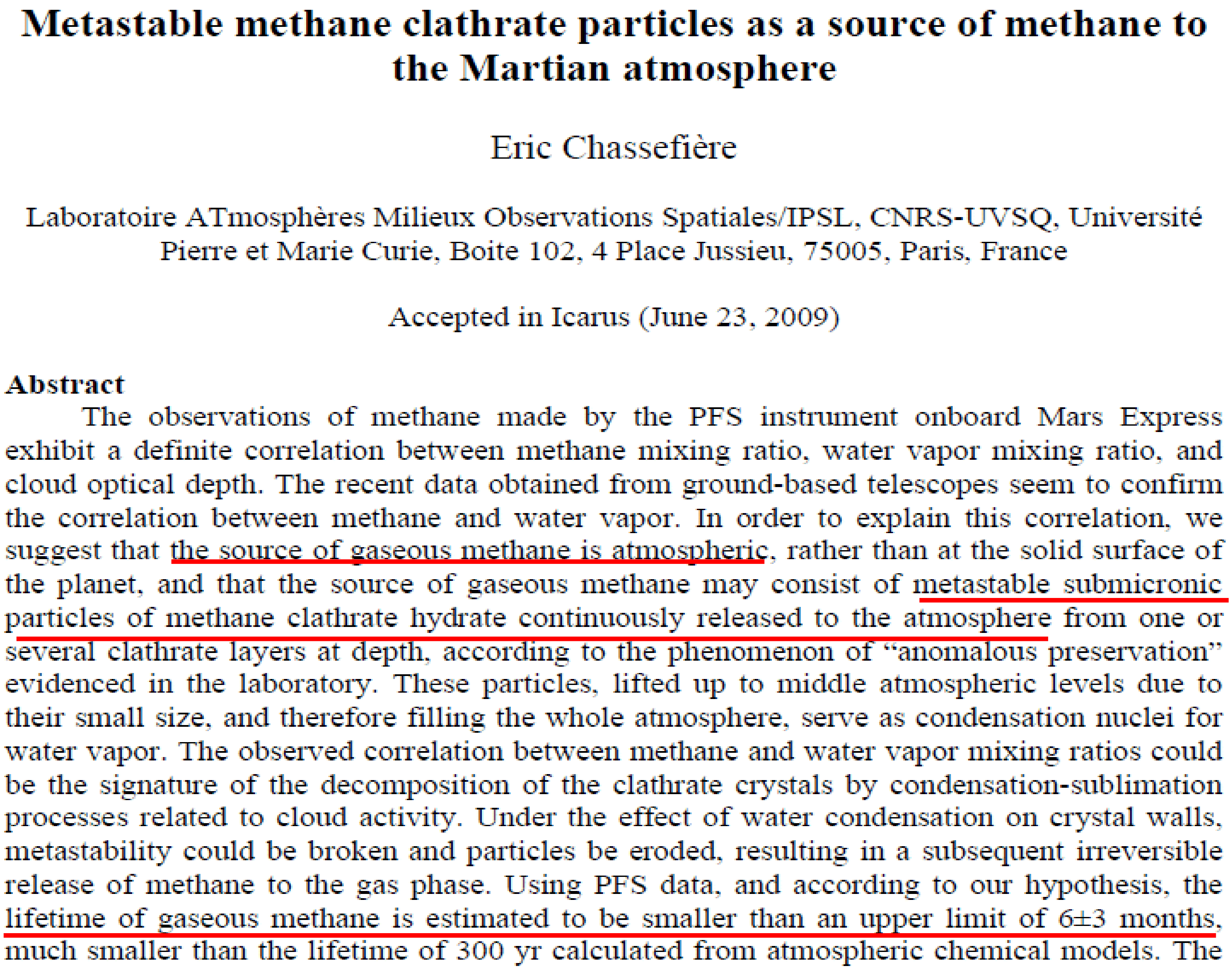
Franck Lefèvre[1] & François Forget[2]

1. LATMOS,
2. Laboratoire de Météorologie Dynamique, UPMC Université Paris 06, CNRS, Paris 75005, France

Correspondence to: Franck Lefèvre[1] Correspondence and requests for materials should be addressed to F.L.
(Email: franck.lefevre@upmc.fr).

The detection of methane on Mars[1, 2, 3] has revived the possibility of past or extant life on this planet, despite the fact that an abiogenic origin is thought to be equally plausible[4]. An intriguing aspect of the recent observations of methane on Mars is that methane concentrations appear to be locally enhanced and change with the seasons[3]. However, methane has a photochemical lifetime of several centuries, and is therefore expected to have a spatially uniform distribution on the planet[5]. Here we use a global climate model of Mars with coupled chemistry[6, 7, 8] to examine the implications of the recently observed variations of Martian methane for our understanding of the chemistry of methane. We find that photochemistry as currently understood does not produce measurable variations in methane concentrations, even in the case of a current, local and episodic methane release. In contrast, we find that the condensation–sublimation cycle of Mars' carbon dioxide atmosphere can generate large-scale methane variations differing from those observed. In order to reproduce local methane enhancements similar to those recently reported[3], we show that an atmospheric lifetime of less than 200 days is necessary, even if a local source of methane is only active around the time of the observation itself. This implies an unidentified methane loss process that is 600 times faster than predicted by standard photochemistry. The existence of such a fast loss in the Martian atmosphere is difficult to reconcile with the observed distribution of other trace gas species. In the case of a destruction mechanism only active at the surface of Mars, destruction of methane must occur with an even shorter timescale of the order of ~1 hour to explain the observations. If recent observations of spatial and temporal variations of methane are confirmed, this would suggest an extraordinarily harsh environment for the survival of organics on the planet.

The last paper: E.Chassefiere



Metastable methane clathrate particles as a source of methane to the Martian atmosphere

Eric Chassefière

Laboratoire ATmosphères Milieux Observations Spatiales/IPSL, CNRS-UVSQ, Université
Pierre et Marie Curie, Boite 102, 4 Place Jussieu, 75005, Paris, France

Accepted in Icarus (June 23, 2009)

Abstract

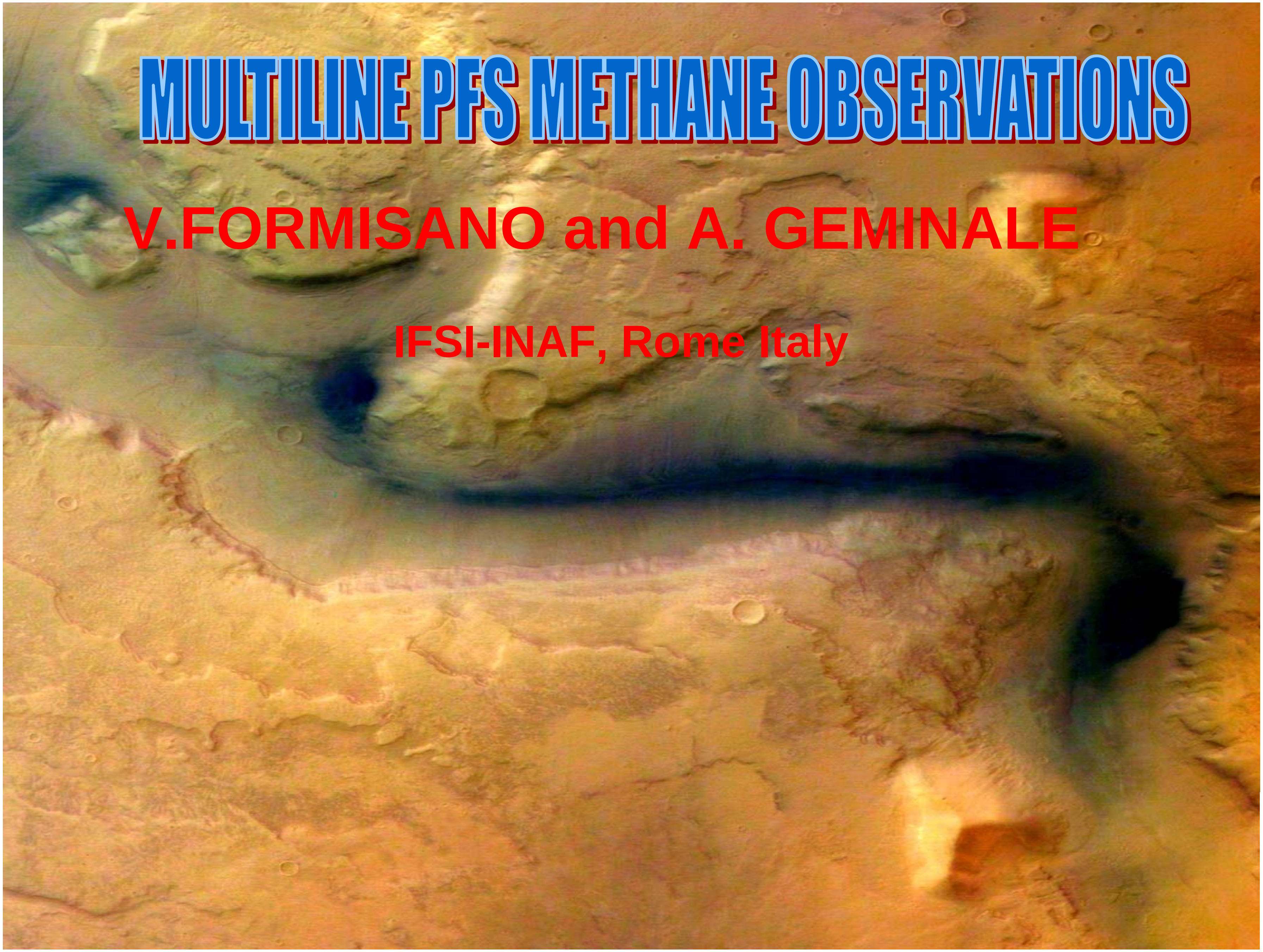
The observations of methane made by the PFS instrument onboard Mars Express exhibit a definite correlation between methane mixing ratio, water vapor mixing ratio, and cloud optical depth. The recent data obtained from ground-based telescopes seem to confirm the correlation between methane and water vapor. In order to explain this correlation, we suggest that the source of gaseous methane is atmospheric, rather than at the solid surface of the planet, and that the source of gaseous methane may consist of metastable submicronic particles of methane clathrate hydrate continuously released to the atmosphere from one or several clathrate layers at depth, according to the phenomenon of "anomalous preservation" evidenced in the laboratory. These particles, lifted up to middle atmospheric levels due to their small size, and therefore filling the whole atmosphere, serve as condensation nuclei for water vapor. The observed correlation between methane and water vapor mixing ratios could be the signature of the decomposition of the clathrate crystals by condensation-sublimation processes related to cloud activity. Under the effect of water condensation on crystal walls, metastability could be broken and particles be eroded, resulting in a subsequent irreversible release of methane to the gas phase. Using PFS data, and according to our hypothesis, the lifetime of gaseous methane is estimated to be smaller than an upper limit of 6±3 months, much smaller than the lifetime of 300 yr calculated from atmospheric chemical models. The

questions

- Where is the source of methane?
- What is the mechanism producing methane? (life or serpentinization).
- Is methane produced today, or is “old” and stored?
- What is the sink of methane?

PFS main objective for this workshop

- 1- Study in detail PFS spectra to show how many methane lines PFS is able to measure.
- 2- Study methane at limb : in order to be able to study in details the relationship between water vapor and methane.
- 3- Map methane in the four seasons in order to study the source-origin of methane.
- 4- study H_2O_2 as a possible oxidiser of methane.
- 5- search for C_2H_6 or some equivalent molecule in order to be able to distinguish (possibly) between serpentinization and life.

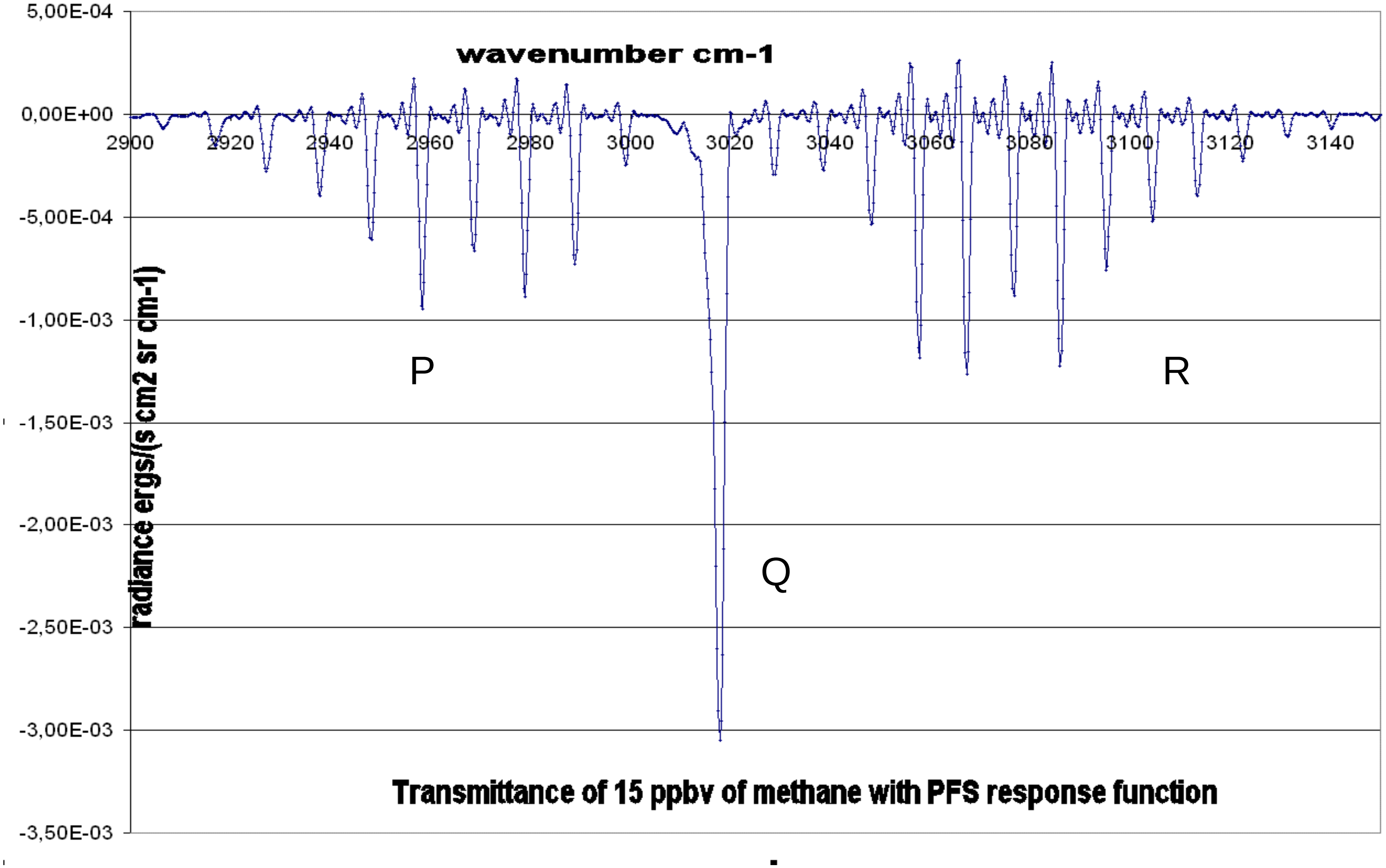


MULTILINE PFS METHANE OBSERVATIONS

V.FORMISANO and A. GEMINALE

IFSI-INAF, Rome Italy

Blow up around the 3018 cm-1 Q-branch



The question is: is PFS able to see any of the P/R branch lines?

The method used

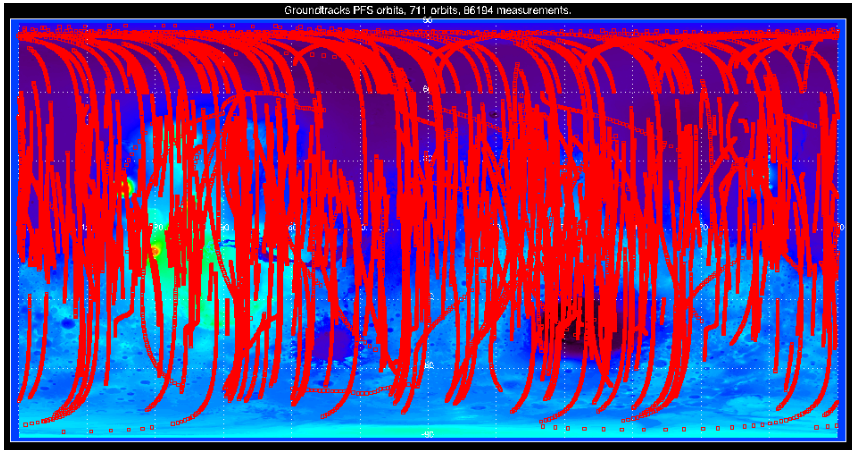
- We shall proceed in the following way:
  - – 1. We first compute orbital averages (700 orbits included) then average all of them using more than one year of data, in total 89000 spectra. In this average the Q-branch depth was of the order of 0.7 % of the continuum.
  - – 2. we then select orbital averages requesting that the Q-branch methane line depth be larger than 1% of the continuum (average over 27000 spectra) and again larger than 2% of the continuum (average over 5200 spectra).

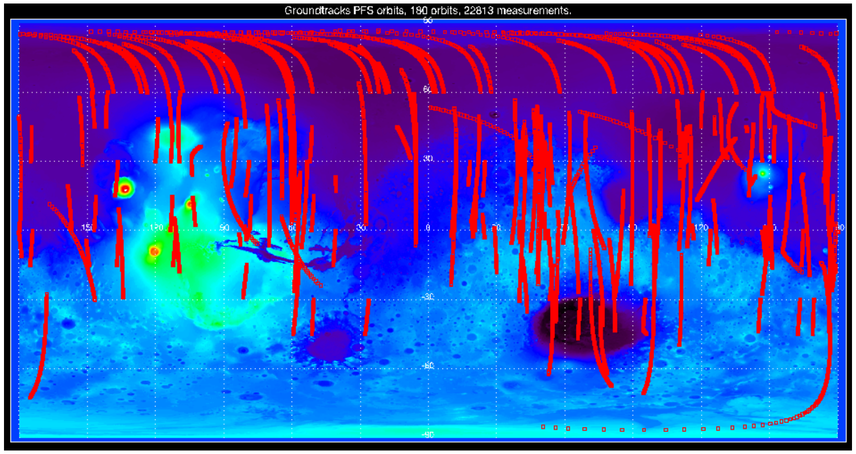
The method used

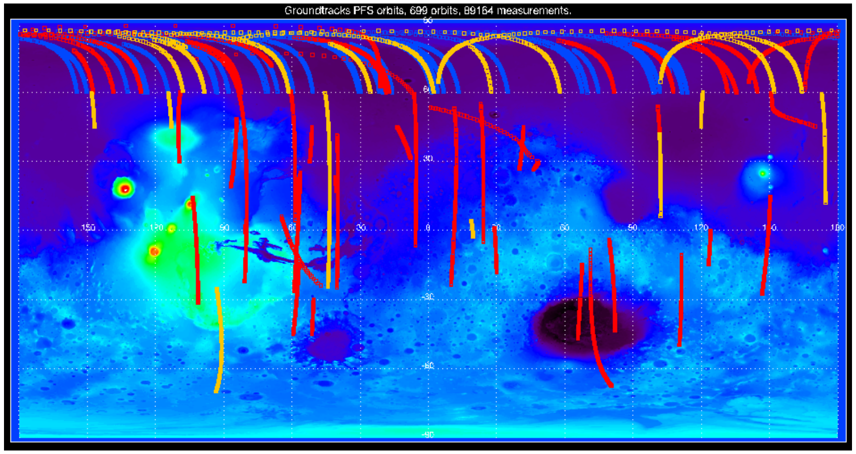
As consequence of our selection all methane lines should be enhanced toghether with the Q-branch in the average of 27000 spectra and in the average of the 5200 spectra.The lines from other gases could roughly remain constant.

The best fit in the 3000- 3030 cm-1 range provides 15 ppbv and 25 ppbv and 35 ppbv respectively for the first ,second and third big average.

Space distribution of the orbits contributing to the 3 averages



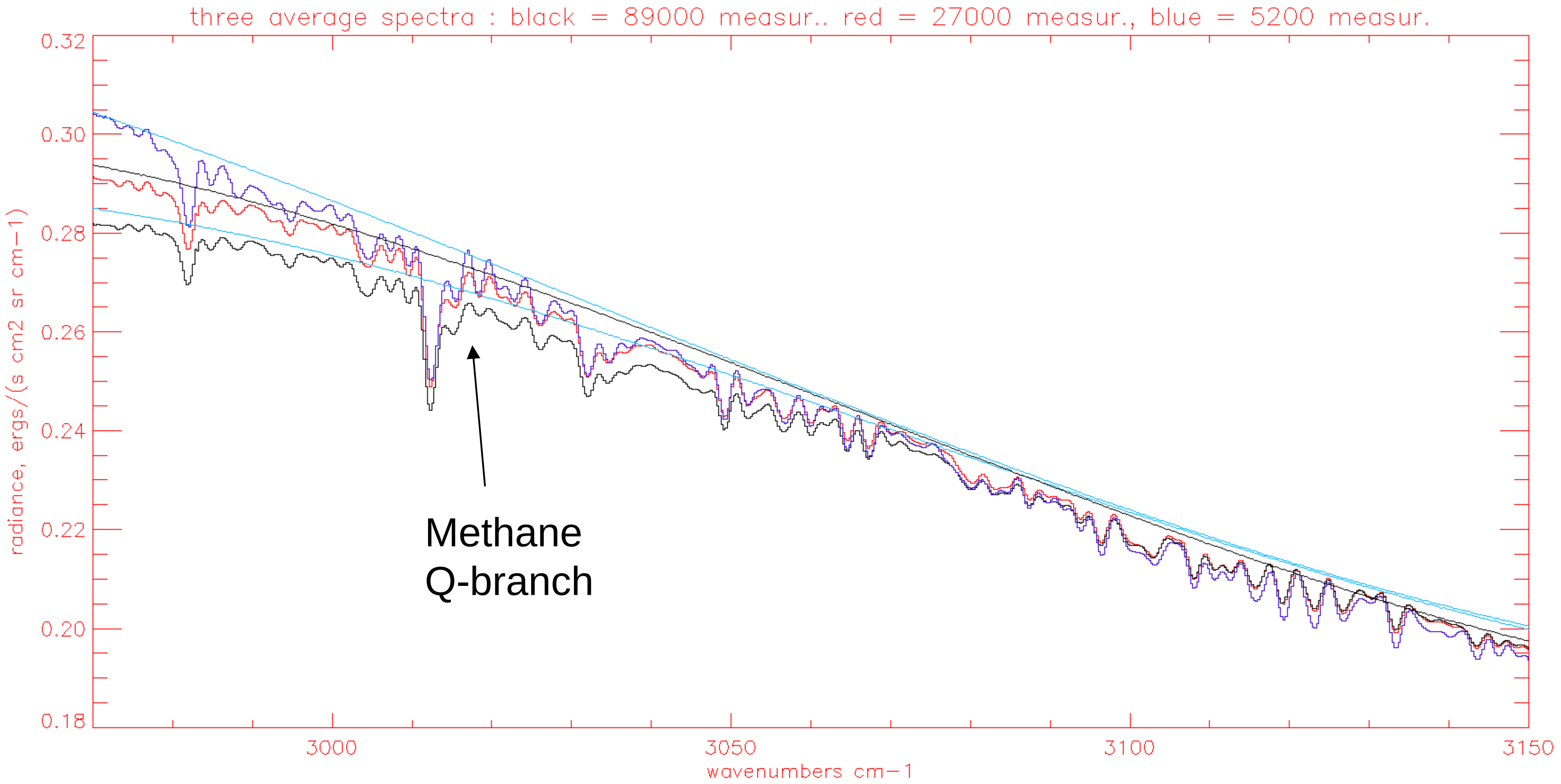




The first map shows the general distribution of the data.

The last map shows regions with most abundant methane (not only the source, but also the enhancement due to CO2 condensation).

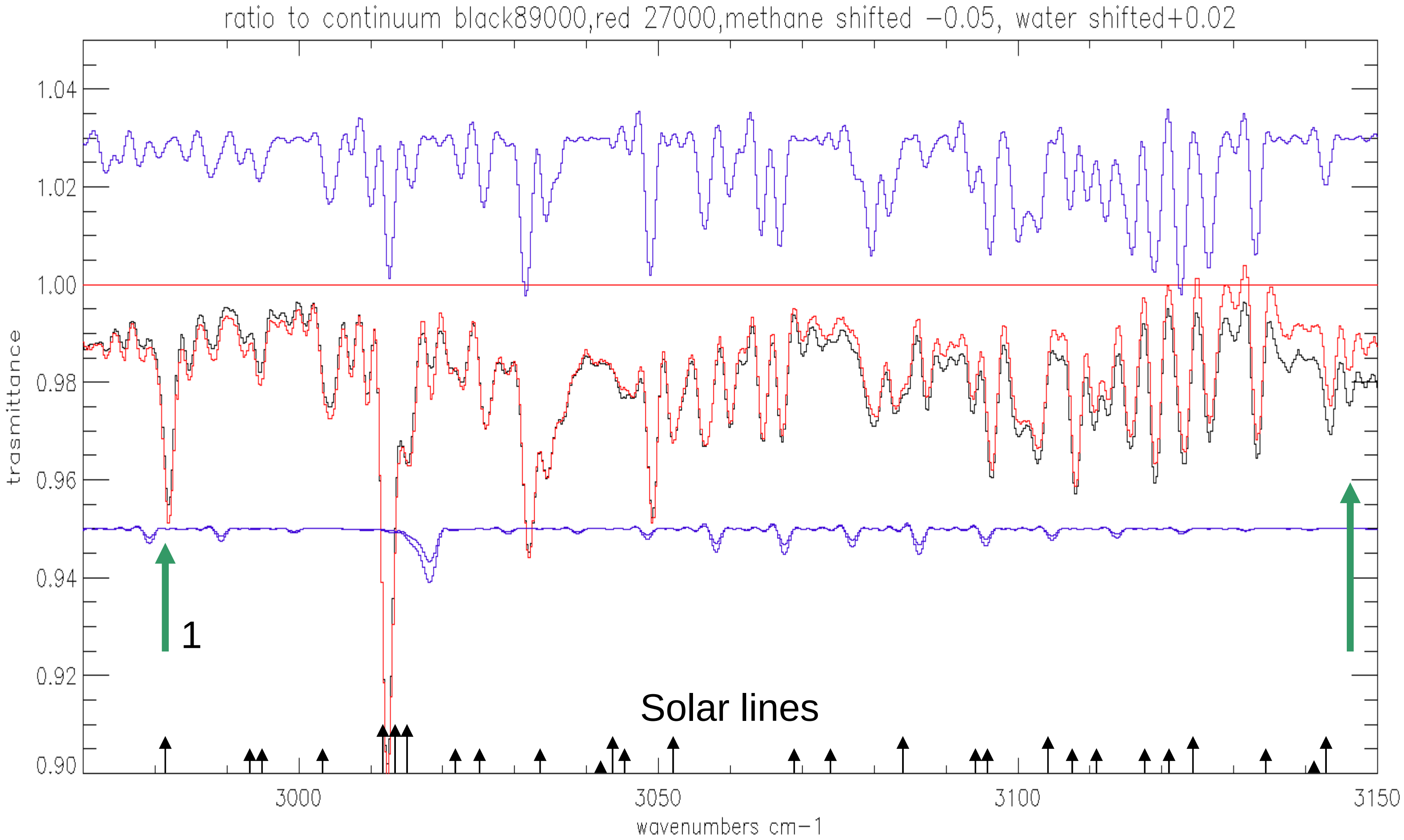
The 3 spectra



Methane
Q-branch

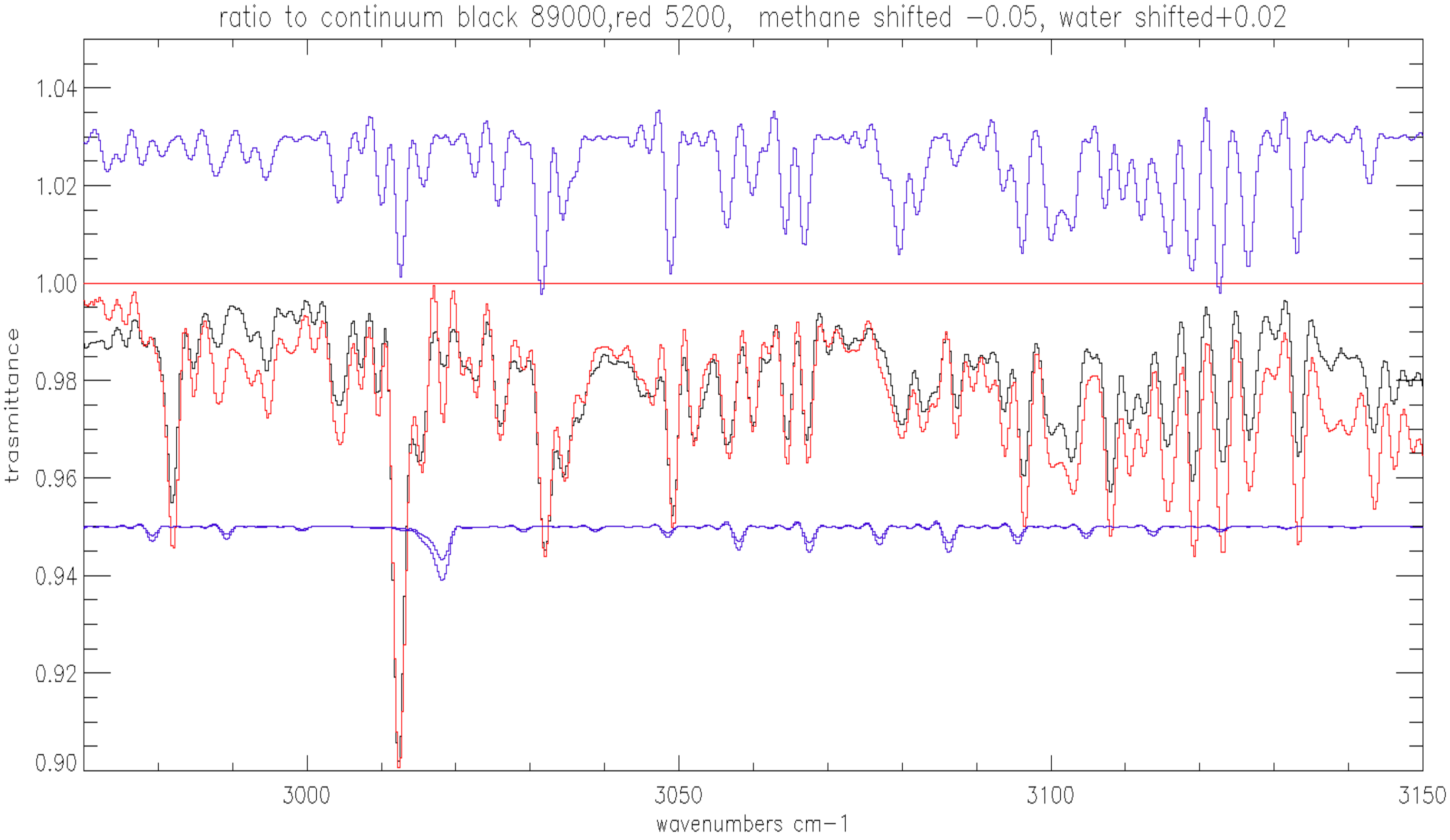
Here the three spectra are shown toghether with the continuum that will be used to compute the trasmissivity of the atmosphere for the minor lines.

Measured trasmissivity compared with water and methane trasmissivity: the first enhancement

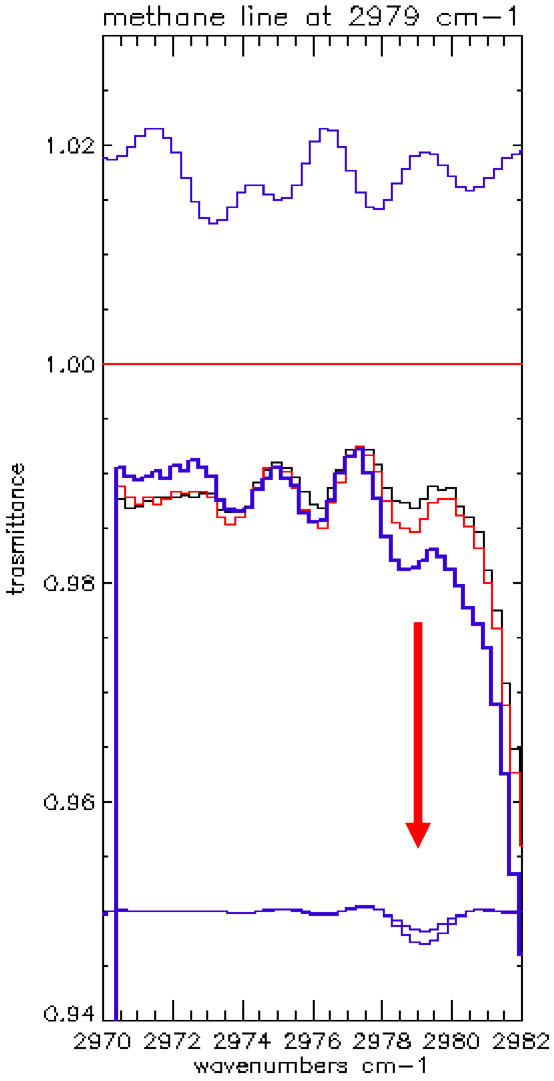


In green major unidentified lines. 1) is 628 CO_2 Q-branch (see Geminale and Formisano, 2008.

Measured trasmissivity compared with water and methane trasmissivity: the second enhancement

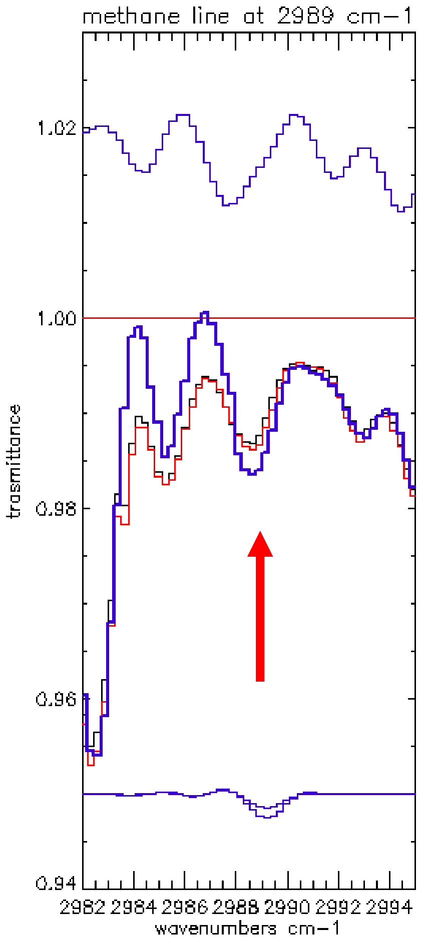


The first line: at 2979 cm-1

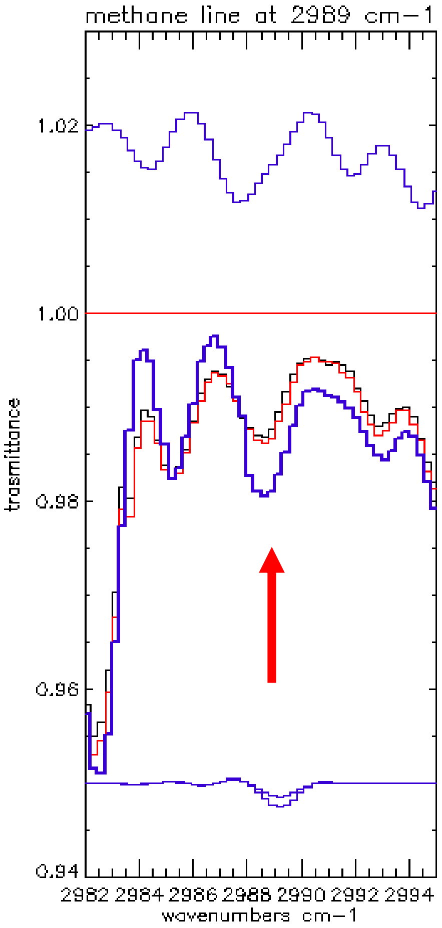


- The first methane line is the P3 line also observed by Mumma. It is just before the 628 isotopologue Q-branch at 2982 cm-1. It is clearly seen to increase intensity as we go from black (average over 89000) to red (average over 27000) to thick bleu (average over 5200).
- At 2976 cm-1 there should be the C_2H_6 etane line, nothing seems to be present.

The second line: at 2989 cm-1



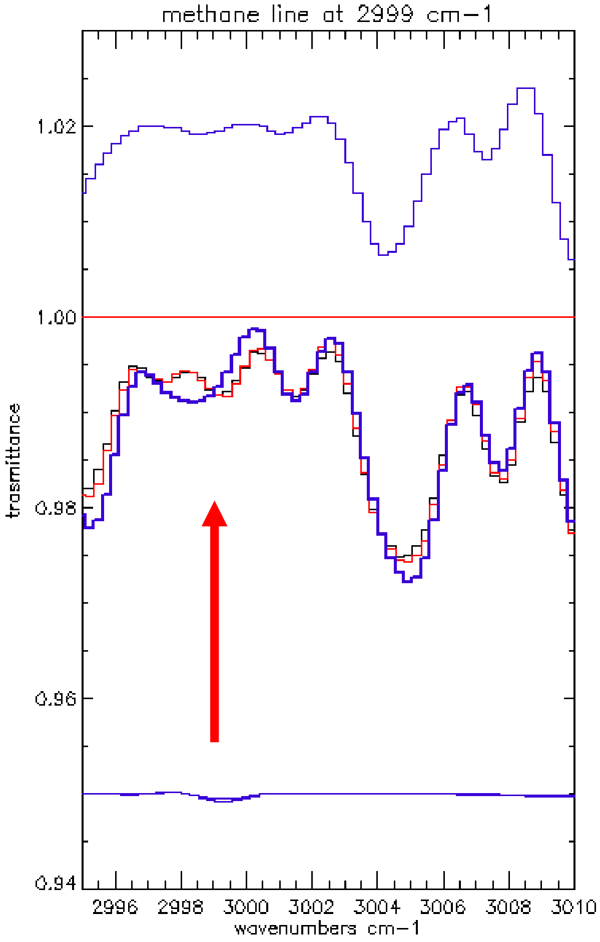
a



b

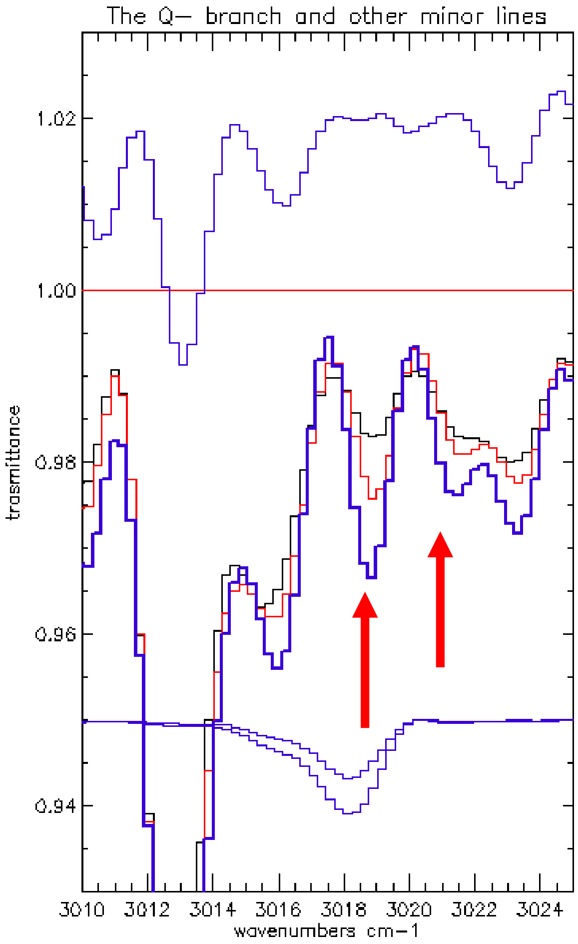
- The second line is smaller, but still clearly visible as a small enhancement in the red curve and as a major difference in the bleu thick curve.
- In the 2 figures a and b are shown two possible matching of the bleu curve to the others : either on the right (2990-2995 cm-1), or on the left (2985cm-1). In both cases the second methane line (the P2) is evident in the transmittance.

The third line:at 2998.5 cm-1



- This is the P1 line. It has still lower intensity then the other two. It is clearly visible in the bleu thick curve, while was not really visible in the red curve.
- The rest of the spectrum in this wavenumber range shows just some minor water lines.

The Q-branch, but not only

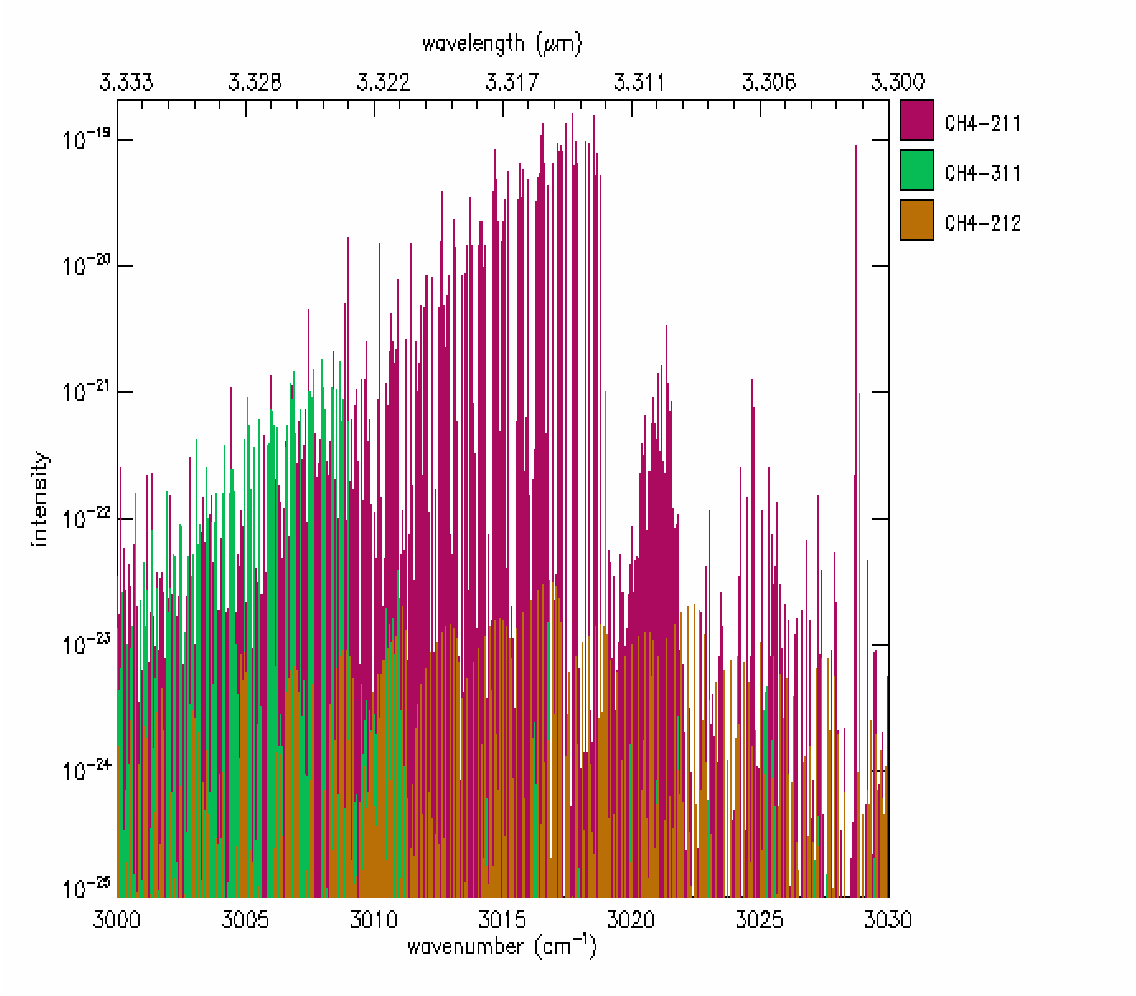


The Q-branch at 3018 cm-1 is the one that we have been requesting to increase from the average intensity of the order of 0.7% or less, to more than 1% (red curve) and more than 2% (bleu thick curve). Its measured intensity is :

- Black curve =0.994-0.983 = 0.7%
- Red curve = 0.994- 0.975 = 1.5 %
- Bleu curve = 0.995 – 0.966= 2.9%

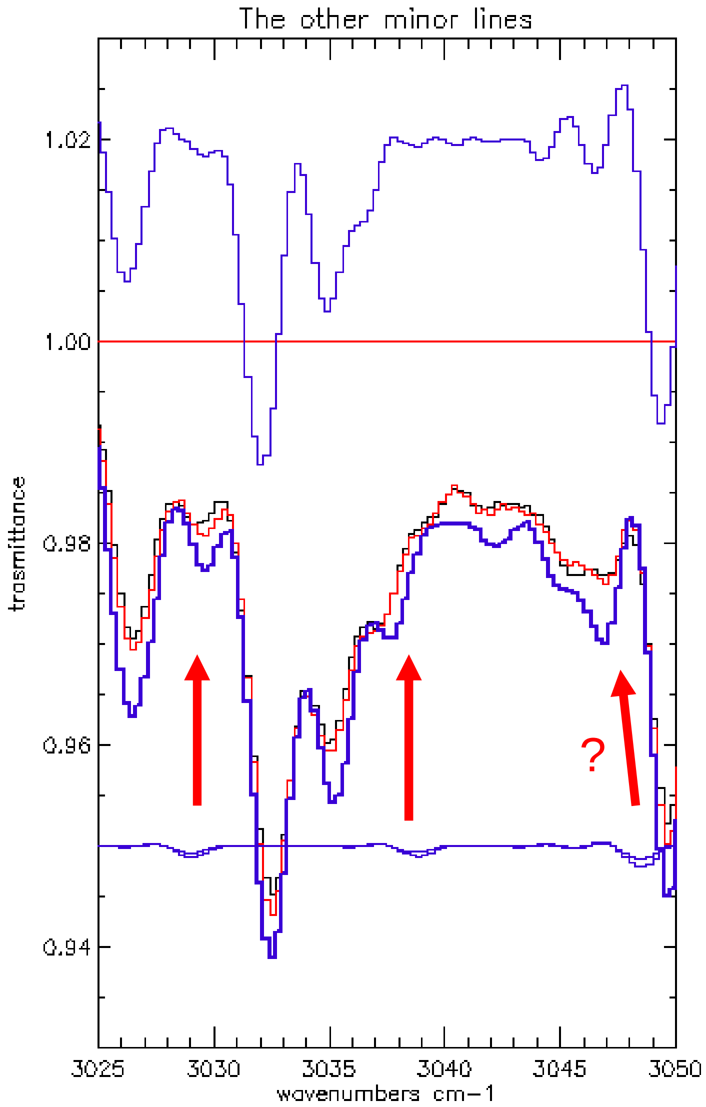
There are other lines' enhancement but they may be due to water vapor, although from the rest of the spectrum it seems water vapor has not changed. A possibility (not demonstrated) is shown in the next figure.

The Q-branch and more: Hitran



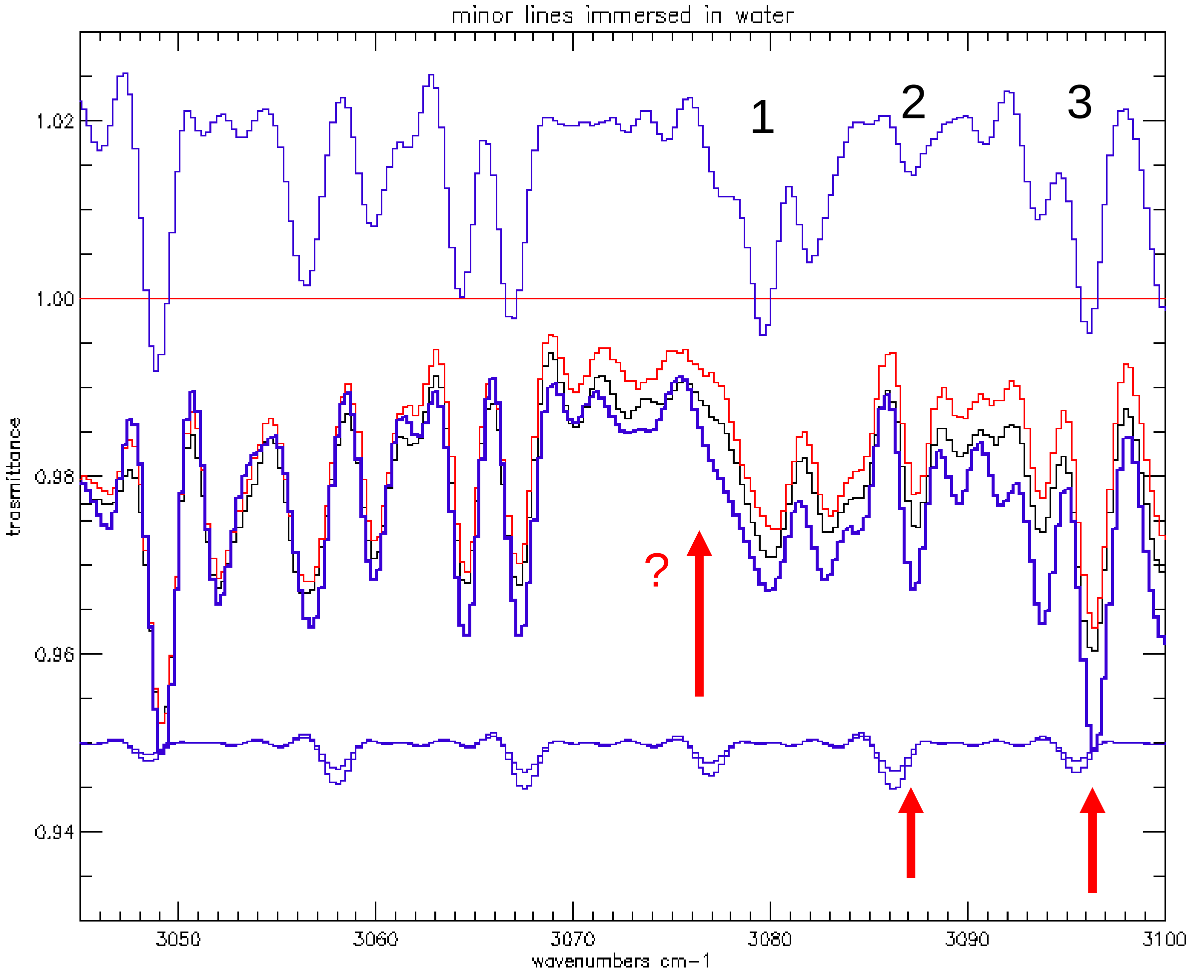
- -This figure shows the Hitran database near the methane Q-branch.
- -The peak of intensity occurs between 3016 and 3019 cm-1, with line intensities of the order of 10^{-19}, but at 3020-3021 cm-1 there is another Q-branch with a much higher lines density, and with lower intensities of the order of 2-4 $*10^{-21}$.
- -A possible interpretation for the feature at 3021 cm-1 is as due to contribution from water vapor, plus an important contribution from this second Q-branch. Note that from the rest of the spectrum we have indication of only a minor water vapor mixing ratio variation, at least for the red curve.

Line number six,seven and eight



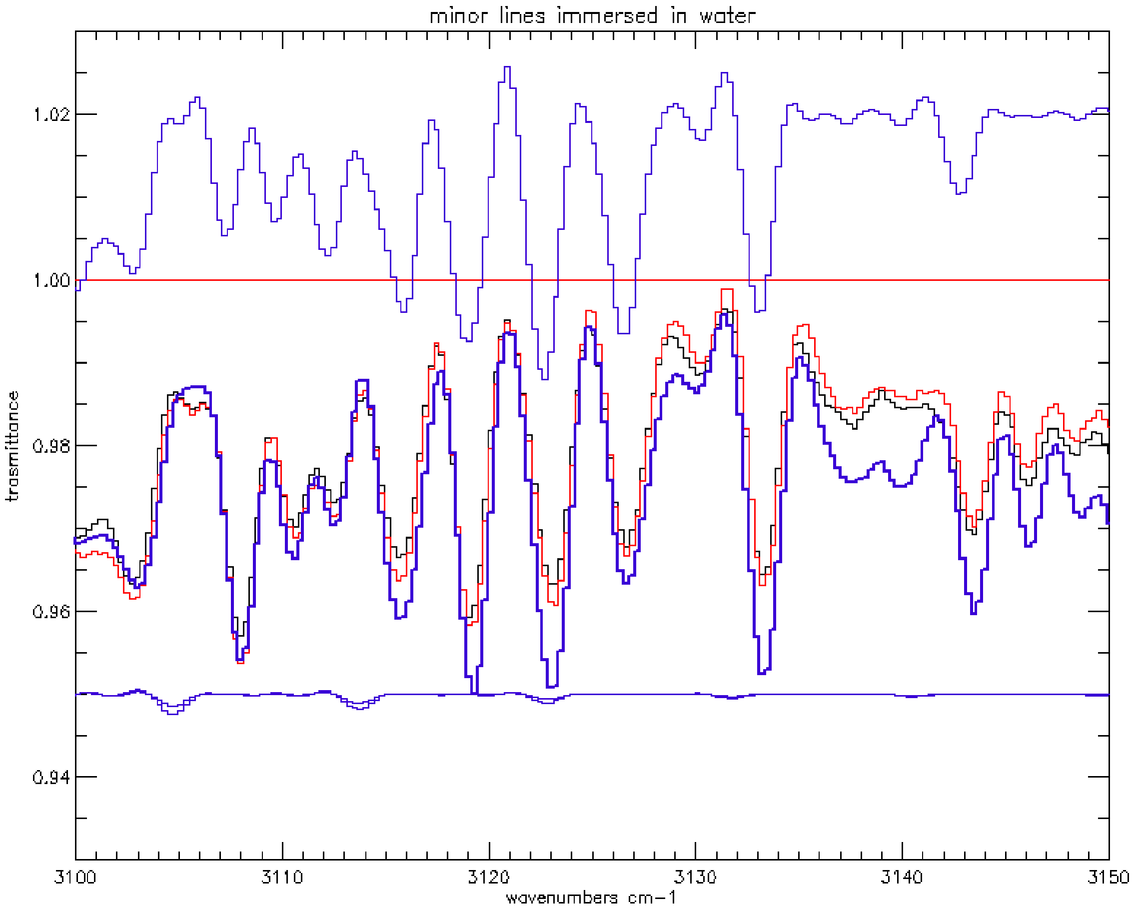
- These are now the R 1, 2, 3 lines. They are still minor lines, but they are clearly visible in all 3 curves, and they are enhanced toghether with the Q-branch.The line at 3038 cm-1 is not well separated, and it is seen after the water line + shoulder. The line at 3049 cm-1 seems to be shifted by 1 cm-1, but this may simply be the effect of the response function of the interferometer, which is a sinc – like function .

Line nine and ten



- Here we have many water vapor lines disturbing the observations, therefore we must compare the observed line intensity with the water synthetic line intensity: with reference to line 1,2, 3, we see that 2 should be much less intense than 1, if would be only water. Observed has the same intensity as 1.
- The line 3 should have the same intensity as 1, but in reality is much more intense.
- In both cases the strong methane lines at 3086 and 3097 cm-1 are contributing to the observed transmittance.

No more lines identified immediately

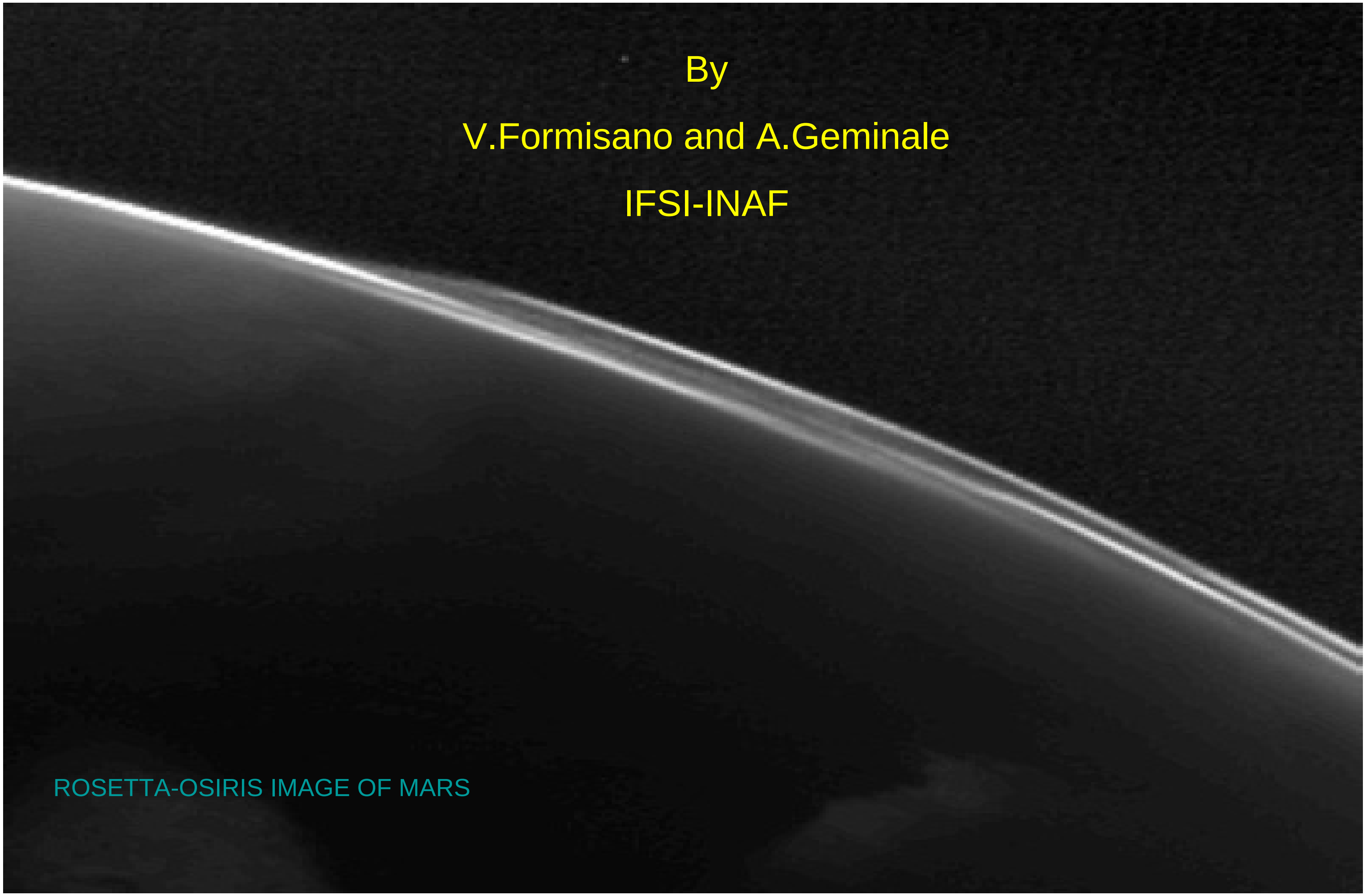


- Several water vapor lines are present in this interval and they mask the methane lines .

Conclusions

- By studying 3 spectra with enhanced methane (mixing ratio of 15, 25, 35 ppbv) we can show that minimum 4, maximum 9 lines on top of the principal Q-branch are observed , mainly when they do not coincide with minor water lines.
- As the soil albedo can be considered a continuum of the spectral region studied (albedo bands due to rocks have usually a wide wavenumber range and not just a couple of cm-1), and because we have been studying the transmittance (soil and aerosols are canceled out), the methane variation cannot be attributed to rocks reflectance effect, but are real variations due to possible short methane lifetime.

Methane at limb with PFS-MEX



By

V.Formisano and A.Geminale

IFSI-INAF

ROSETTA-OSIRIS IMAGE OF MARS

The data set

- Spring 23 orbits
- Summer 25 orbits
- Fall 23 orbits
- Winter 23 orbits
- All orbits are special in the sense that the IFOV never looks at the soil, and we usually have more than 70 measurements at different altitudes.
- Altitude 0-50 Km
- Limb distance< 3000 Km
- Total number of spectra = 4114

The data set:number of spectra

Altitude Km	5	15	25	35	45
Spring	445	132	156	200	167
Summer	257	102	480	325	184
Fall	505	93	87	79	70
Winter	389	81	112	125	125
Total	1596	408	835	729	546
Grand total					4114

The altitude of a measurement is computed as the altitude of the optical axis of the instrument minus half the IFOV.

Method of study

1- Average all the data between 0-10 Km (or 10-20, 20-30, 30-40, 40-50 Km) altitude in one season.

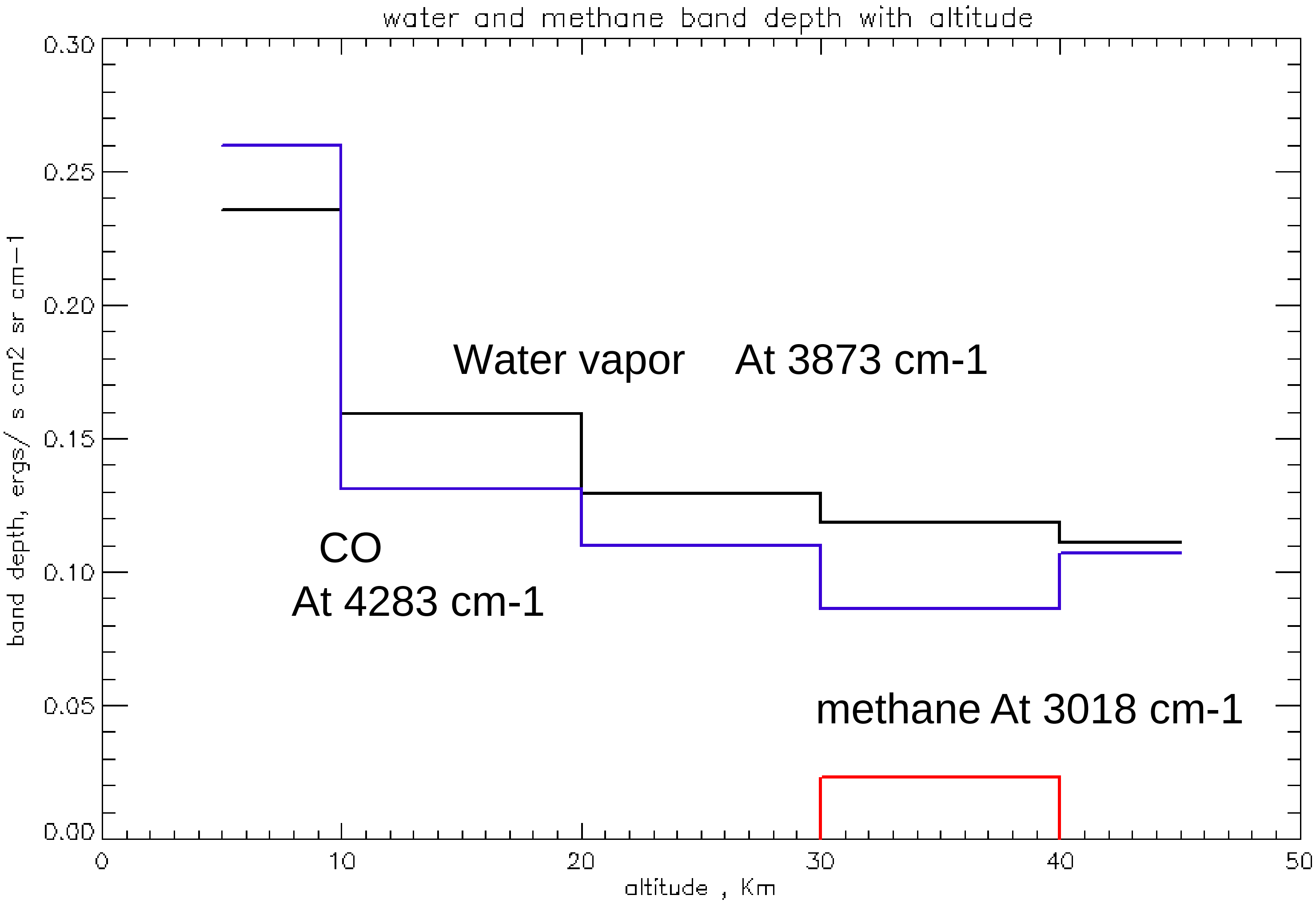
2- Measure the line depth= $(I_{max} - I_{min})/I_{max}$, which is proportional (almost) to the equivalent width and therefore to the column density.

3- Consider water vapor (3783 cm-1), CO (4283 cm-1) methane(3018 cm-1) lines and the aerosols as continuum at 7100, 4000 and 2800 cm-1).

4- Plot the measured quantities as function of altitude.

5- Study all possible geometrical parameters to identify possible bias (latitude, phase angles etc.).

Vertical profile of water, CO, and methane in spring



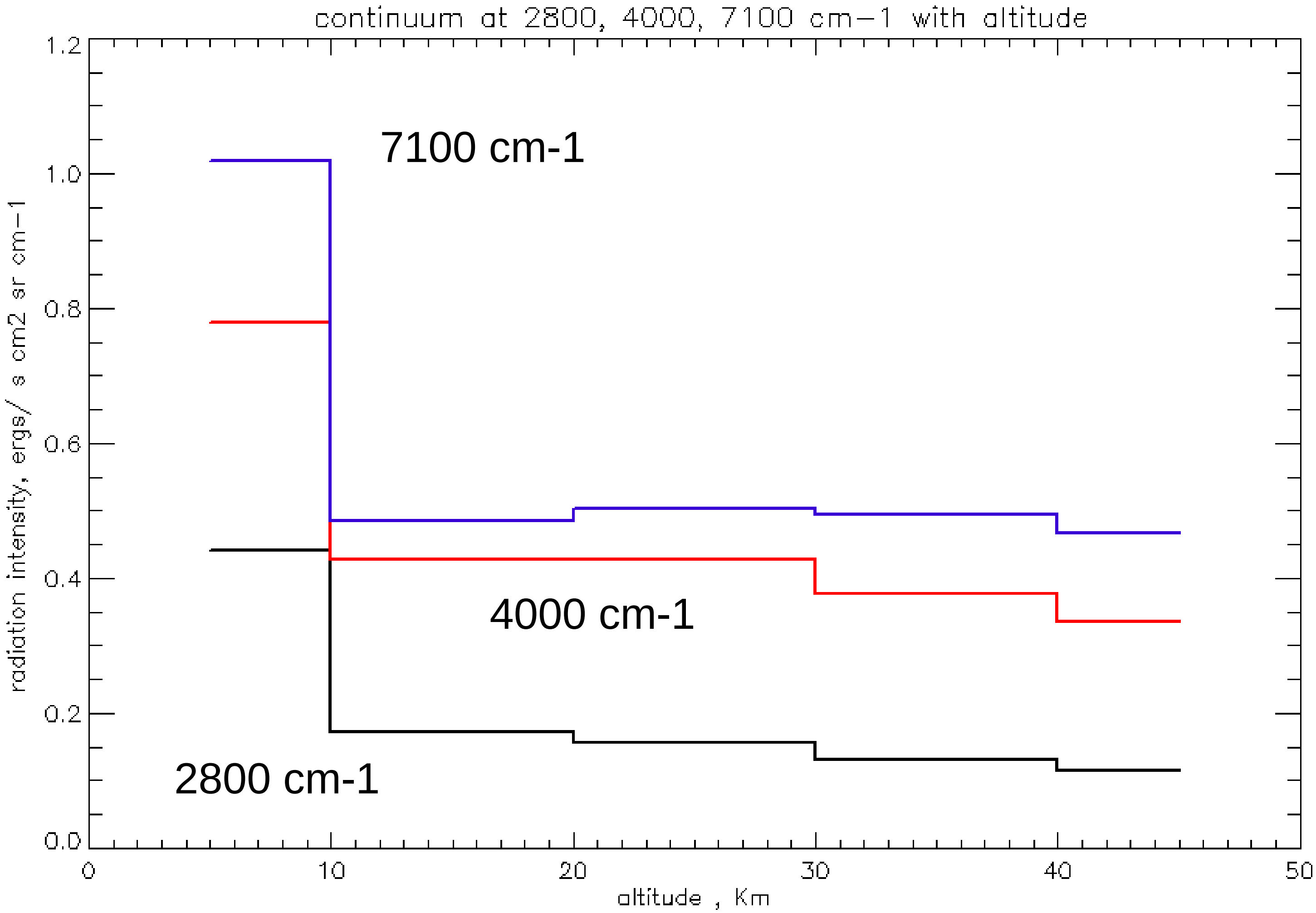
Water vapor At 3873 cm-1

CO
At 4283 cm-1

methane At 3018 cm-1

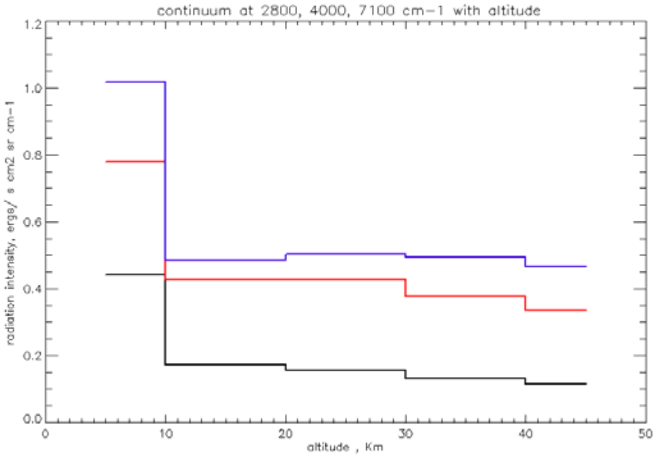
Band depth as percentage of continuum

Vertical profile of continuum in spring

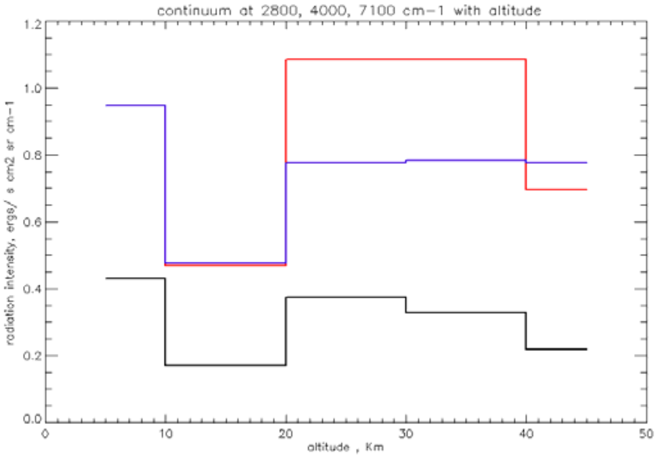


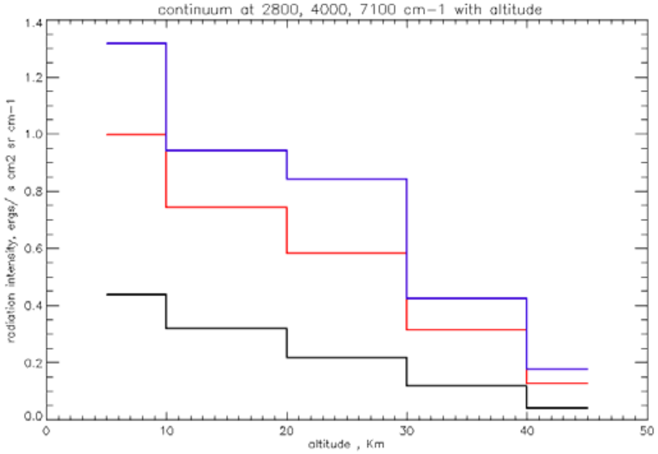
Aerosols comparison in the 4 seasons

Lat= -60 to +60

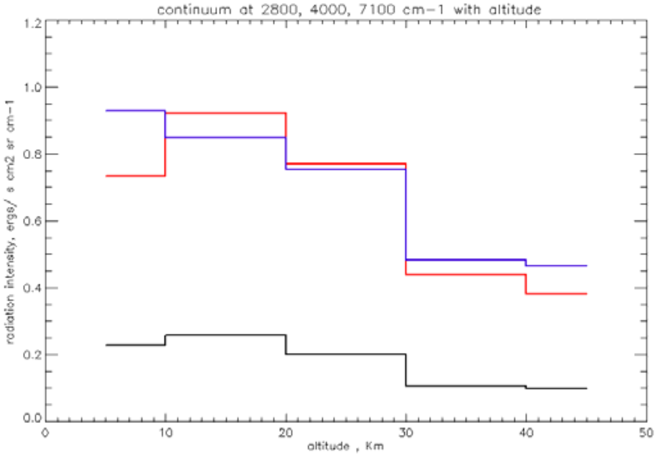


Lat= +10 to +60





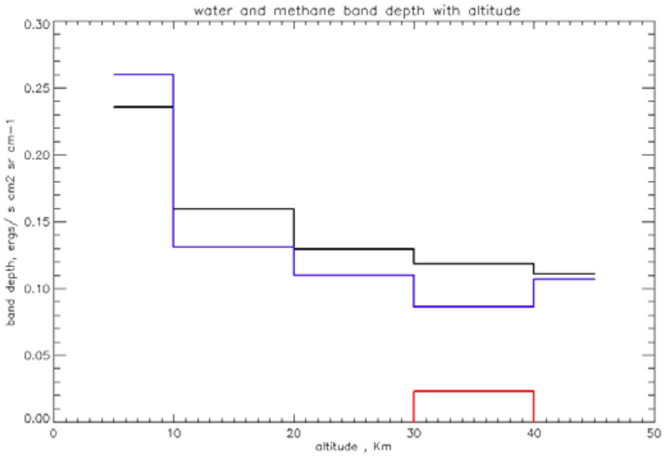
Lat= -60 to +10



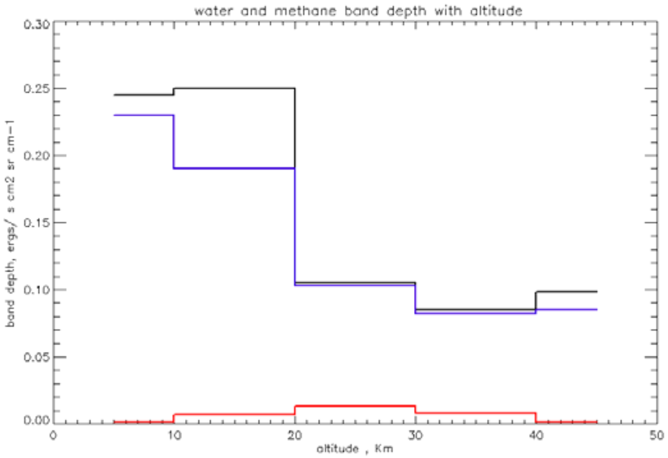
Lat= -60 to +10

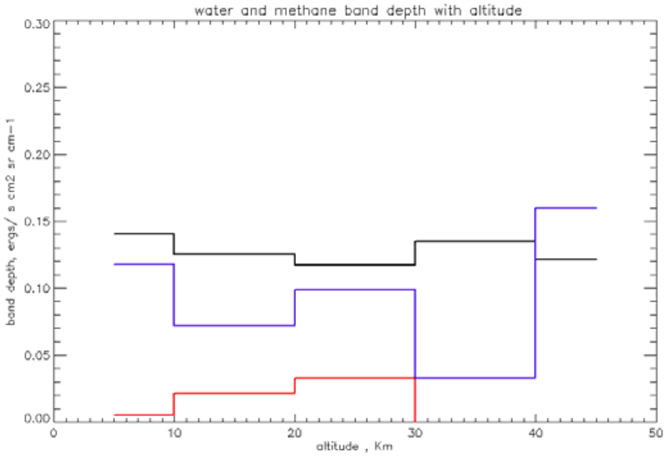
Gases profiles in the 4 seasons

spring

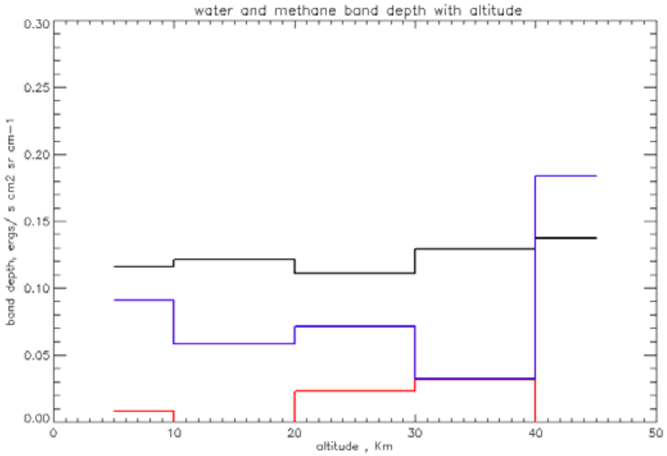


summer





autumn



winter

conclusions

- 1- There is no correlation between the vertical profile of water vapor and methane.

- 2- The maximum abundance of methane is not observed close to the soil, but in the middle of the atmosphere at 25-35 Km. Therefore methane has an unusual vertical abundance profile.This fact has, as consequence, that it is better to speak of column density for methane, and not of mixing ratio, because this quantity is changing with altitude.

- 3- Only in Autumn (and perhaps in winter) the aerosols in the atmosphere do not extend above 50 Km altitude.

conclusions

- 4- Water vapor has its maximum band depth close to the soil in spring and summer, while is vertically uniform in autumn and winter.
- 5- CO has its maximum band depth close to the soil in spring and summer, while in autumn and winter has its maximum at very high altitudes.
- 6- Except than in autumn and winter, in the other seasons the aerosols clearly extend much above the 50 Km altitude.
- 7-The methane behaviour can be explaned by the Chassefiere theory.

»THE END