Abstract Book & Programme

25- 27 November 2009
European Space Agency
ESRIN
Frascati, Italy

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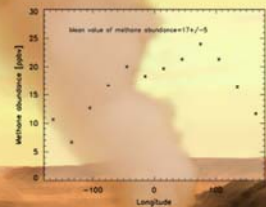
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Workshop secretariat:

ESA Conference Bureau
European Space Agency ESRIN
Via Galileo Galilei
Casella Postale 64
00044 Frascati (Roma)
Italy
Esa.conference.bureau@esa.int

Wednesday 25 November 2009

9:00-10:00: Registration, posters set up, coffee

09:45 – 10:00 Welcome and opening (ESA, ASI)

Session 1 - Observations of methane from orbit
Moderator: O. Witasse

10:00-10:35   Methane observations with PFS-MEX: an introductory historical overview, multiline observations and limb measurements (solicited)
Formisano, V.

10:35-10:50   PFS-MEX: Mapping methane in Martian atmosphere
Geminale, A.

10:50-11:05   Spatial distribution and temporal evolution of methane in the Martian atmosphere
Fonti, S.

Session 2: Ground-based observations of methane
Moderator: O. Witasse

11:05-11:25   Absolute measurements of Methane on Mars (solicited)
Mumma, M.

11:25-11:45   Methane and water on Mars: Maps of active regions and their seasonal variability (solicited)
Villanueva, G.

11:45-12:15   Coffee break

12:15-12:35   Measurement of the isotopic signatures of water on Mars: implications for studying methane (solicited)
Novak, P.

12:35-12:40   Poster presentation (3 minutes): High Spectral resolution heterodyne spectroscopy of methane at 7.8 µm
Sonnabend, G.

Session 3: Martian surface and subsurface data, and laboratory measurements relevant to the study of methane
Moderator: P. Mahaffy

12:40-12:55   Mapping ice deposits on Mars through subsurface radar sounding (solicited)
Orosei, R.

12:55-13:15   Morphology and Mineralogy of Methane Source Regions (solicited)
Wray, J.

13:15-13:30   The search for methane gas emission features in Nili Fossae, Syrtis Major, and Isidis Planitia, Mars
Komatsu, G.

13:40 Lunch

14:50-15:15 Surface conditions from thermodynamics of phyllosilicates and implications for the presence of methane on early Mars (solicited)
Chevrier, V.

15:15-15:35   Laboratory investigation of the role of heterogeneous processes in Martian methane variability (solicited)
Gough, R.

15:35-16:25 Discussion on the data sets available (from orbit, ground-based measurements, laboratory measurements, other data sets of interest)

16:25-16:55 Coffee break

Session 4: Origin of Martian methane
Moderator: S. Atreya

16:55-17:20   Methane and the Martian Habitability (solicited)
Atreya, S.

17:20-17:40   Production on Mars by photolysis of H_2O in the presence of CO (solicited)
Bar-Nun, A.

17:40-18:00   Methanogenesis in Terrestrial Permafrost: a Model for Methane Sources on Mars? (solicited)
Wagner, D.

18:00-18:20   Methane Sources and Sinks: The geobiology of the Arctic versus Mars (solicited)
Onstott, T.

18:20-18:25   Poster presentation (3 minutes): Abiotic methanogenesis carbonate reduction by hydrogen-bearing fluids: a mechanism for Martian methane
Lazar, C.

18:30-19:30   Welcome reception

Thursday 26 November 2009

Session 5: Storage, release, and delivery of methane
Moderator: V. Chevrier

09:00-9:15   Methane reservoirs on Mars: A story of migration, gas hydrates, traps, and a long production cycle
Ori, G.

09:15-09:35   Methane Emissions from Earth's Degassing: a Reference for Mars (solicited)
Etiope, G.

09:35-09:50   Methane hydrates: A source for slow methane release on Mars? (solicited)
Elwood-Madden, M.

09:55-10:15   Metastable Methane Clathrate Particles as a Source of Methane to the Martian Atmosphere (solicited)
Chassefiere, E.

10:15-10:25   Poster presentations (3 minutes each)

The trapping of methane in Martian clathrates hydrates
Thomas, C.

Variability of Atmospheric Methane Induced by Adsorption in the Regolith
Meslin, P.-Y.

10:25-11:00   Discussion on origin, storage, release, and delivery of methane

11:00-11:30   Coffee break

Session 6: Atmospheric circulation and chemistry
Moderator: F. Forget and F. Lefèvre

11:30-11:50   Challenges raised by the observed variations of methane on Mars (solicited)
Lefèvre, F.

11:50-12:05   A short-Lived Trace Gas in the Martian Atmosphere: A General Circulation Model of the Likelihood of Methane
Chizek, M. R.

12:05-12:20 Argon: The Mixing Standard for Methane in Mars Atmosphere
Sprague, A. L.

12:20-12:35   The spatial and temporal variation of oxidant component in the Martian atmosphere observed by MEX/PFS
Aoki, S.

12:35-12:50   Unusual CO behaviour in Martian atmosphere: a relation to methane?
Formisano, V.

12:50-13:05   Photochemically induced formation of Mars-relevant oxygenates and methane from carbon dioxide and water
Wecks, M.

13:05-13:25   Poster presentations (3 minutes each)

The photochemistry and atmospheric lifetime of methane on Mars for evolving atmospheric concentrations of carbon dioxide and the variability of the Mars planetary boundary layer (PBL) based on measurements from the Viking 1 and 2 landers, Mars Pathfinder and Phoenix.
Levine, J.

Mars atmospheric circulation and chemistry detected in the submm domain
Hartogh, P.

Search for important minor gases in Martian atmosphere
Geminale, A.

Search for hydrogen peroxide in the Martian atmosphere
Formisano, V.

Search of SO2 in the Martian atmosphere by ground-based submillimeter observation
Nakagawa, H.

The Formaldehyde Observation of 1969 and 1989: Analyses of the Observations and Proposals for Interpretation
Muller, C.

13:25-13:50   Discussion on the atmosphere circulation and chemistry

13:50 Lunch

Session 7: Microbial life, metabolism in water ice, and biological experiments under Martian conditions
Moderator: B. Price

14:55-15:15 (solicited)
Price, B.
Microbial Life in Ice: Habitats, Metabolism, and Survival on Mars

15:15-15:30
Prieur, D.
Methanogenesis on Earth Today: Where, Who and How

15:30-15:45 respiration
Coates, J.D.
The possibility of methane oxidation coupled to microbial perchlorate

15:45-16:00
Whyte, L.
A sub-zero high Arctic methane seep: implications for Mars methane

16:00-17:30 Coffee break and poster session

List of posters:

1. High Spectral resolution heterodyne spectroscopy of methane at 7.8 µm
Sonnabend, G.

2. Abiotic methanogenesis carbonate reduction by hydrogen-bearing fluids: a mechanism for Martian methane
Lazar, C.

3. The trapping of methane in Martian clathrates hydrates
Thomas, C.

4. Variability of Atmospheric Methane Induced by Adsorption in the Regolith
Meslin, P.-Y.

5. The photochemistry and atmospheric lifetime of methane on Mars for evolving atmospheric concentrations of carbon dioxide and the variability of the Mars planetary boundary layer (PBL) based on measurements from the Viking 1 and 2 landers, Mars Pathfinder and Phoenix.
Levine, J.

6. Mars atmospheric circulation and chemistry detected in the submm domain
Hartogh, P.

7. Search for important minor gases in Martian atmosphere
Geminale, A.

8. Search for hydrogen peroxide in the Martian atmosphere
Formisano, V.

9. Search of SO_2 in the Martian atmosphere by ground-based submillimeter observation
Nakagawa, H.

10. The Formaldehyde Observation of 1969 and 1989: Analyses of the Observations and Proposals for Interpretation
Muller, C.

11. Growth and Biomediated Mineral Alterations by Methanogens under Geochemical Conditions Similar to the Martian Subsurface
Chastain, B. K.

12. Determination of the surface concentrations of methane on Mars with MOMA
Steininger, H.

13. Using Laser Heterodyne Radiometry to Search for Methane on Mars
Passmore,R.L.

14. Robotic rigid vacuum airship for exploration of Mars
Pahari, S.

15. Detecting and characterizing Martian dust using spectropolarimeter SPEX
Stam, D.

16. Possible Influences of Aerosol Loading on the Measured Columns of Martian Atmospheric Constituents Including Methane
Muller, C.

DINNER

Friday 27 November 2009

09:00-09:20 Methanogens: A Model for Life on Mars (solicited)
Kral, T.

09:20-09:35   Methanogenic Activity in Rio Tinto, a Terrestrial Analogue of Mars
Amils, R.

09:35-09:50   Bacterial survival in Martian conditions
Galletta, G.

09:50-10:05   Zero-Valent Iron on Mars: an Alternate Energy Source for Methanogens
Chastain, B. K.

10:05-10:15   Poster presentations (3 minutes)

Growth and Biomediated Mineral Alterations by Methanogens under Geochemical Conditions Similar to the Martian Subsurface
Chastain, B. K.

10:15-11:00   Discussion on microbial life

11:00-11:30   Coffee break

Session 8: Future measurements of methane, related trace gases, and isotopes
Moderators: A. Chicarro and R. Zurek

11:30-11:50   Future in situ methane and related trace gas and isotope measurements with the Sample Analysis at Mars (SAM) instrument suite of the 2011 Mars Science Laboratory (MSL) (solicited)
Mahaffy, P.

11:50-12:10   Measuring Methane and its Isotopic Ratios 13C/12C and D/H With the Tunable Laser Spectometer (TLS) on the 2011 Mars Science Laboratory (MSL) Mission (solicited)
Webster, C.

12:10-12:25   Studying methane and other trace species in the Mars atmosphere using a SOIR instrument
Drummond, R.

12:25-12:45   A New Mission Concept: The Search for Atmospheric Trace Gases in the Mars Atmospheric (solicited)
Zurek, R.

12:45-13:05   Posters presentations (3 minutes each)

Determination of the surface concentrations of methane on Mars with MOMA
Steininger, H.

Using Laser Heterodyne Radiometry to Search for Methane on Mars
Passmore,R.L.

Robotic rigid vacuum airship for exploration of Mars
Pahari, S.

Detecting and characterizing Martian dust using spectropolarimeter SPEX
Stam, D.

Possible Influences of Aerosol Loading on the Measured Columns of Martian
Atmospheric Constituents Including Methane
Muller, C.

13:05-13:40   Discussion on future measurements

13:40 Lunch

14:50-16:00 General discussion, conclusions, closure of the symposium
S. Atreya, F. Forget, P. Mahaffy, and O. Witasse

METHANE OBSERVATIONS WITH PFS-MEX : AN INTRODUCTORY HISTORICAL OVERVIEW.

V.Formisano and A. Geminale , IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it).

Abstract: In occasion of the methane workshop to be hold in Frascati on November 25-27, 2009, we shall present the historical overview of the work done on methane. We mention the Krasnopolsky et al [1], and the Mumma et al [2]work, but we shall mostly concentrate on the work done with the PFS-MEX experiment (Science 2004)[3]. With this data we first identified the average methane mixing ratio to be of the order of 10 ppbv. Most important we reported immediately the variability of this quantity from very low values (down to zero ppbv) up to large values (35 ppbv or above). These results have recently been confirmed by Mumma et al.[4], after re-analysis of their ground based measurements. The location with particularly higher methane mixing ratio, reported in the Science paper to be in the wide longitudinal range 20-150 E-longitudes, has also been confirmed by Mumma et al in the 270-330 W-longitudes (= 30 – 90 E-longitudes).

PFS data analysis went on with the study of the variability with seasons, longitude, latitudes and local times (PSS 2007) [5]. Excluding the polar regions, we found that the seasonal variations show the maximum methane intensity in the northern spring, and the minimum in the southern summer. The longitudinal study confirmed the maximum methane at the E-longitude of 80 degrees. No clear behaviour was found with the local time.

In general a relatively good correlation was found with the water vapour, but it was stressed that this should be considered not a real correlation, but rather pointing to the same source.

Several works have been performed and shall be presented to this workshop; they aim to clarify a number of important issues.

A study has been performed to demonstrate that the 3018 cm-1 line studied with PFS data is indeed representative of methane mixing ratio, and that many more methane lines are measured in the PFS spectrum.

Limb measurements should provide the vertical profile of the methane abundance, and by comparing with the vertical water vapour abundance we shall verify either the A. Bar Nun suggestion [6](methane is generated by water vapour photochemistry), or the recent theory of E.Chassefiere (2009) (methane is transported by clathrate hydrate into the atmosphere and then released)[7].

A very important study is then the mapping of methane in Martian atmosphere. This has been done using all seasons data together(850000 of which only 500000 usable), but the number of measurements is not large enough for a good mapping, and only 20^ox20^o latitude longitude mapping can be performed separating the 4 seasons, as we need at least 400 measurements in each box to have a reasonable SNR. In doing these mapps, we have seen the consequences of the 11/5 orbit resonance, which prevents a good distribution of the data over longitudes.

The variability of methane mixing ratio has been linked to a strong oxidiser (H_2O_2), the mixing ratio of this gas, however, is not well know in Martian atmosphere. The strong oxidiser is believed to be confined to the soil dust, being generated during dust storms around dust grains by strong electrostatic fields. A study with PFS data has been made resulting in a mixing ratio of H_2O_2 of 120 ppbv.

Finally a study has been made to evaluate some other minor gases that could help in understanding the mechanism that is generating methane : life or serpentinization or something else. The search for C_2H_6 (which should identify serpentinization) has only produced an upper limit of 10 ppbv. An anomalous behaviour of CO (normally anti-correlated with water vapour) correlated with water vapour sublimating from the northern polar cap in northern summer in special occasions, could indicate life in the ice.

References:

[1] Krasnopolsky V. A. ,Maillard J.P.and Owen T.C. (2004) Icarus*,172,537*. [2] Mumma M.J. et al. (2003) Bull.Am.Astron. Soc., 35, 937,(2003). [3] Formisano V., S.Atreya, T.Encrenaz, N. Ignatiev, M. Giuranna Science 306, 1758 (2004). [4] Mumma M.J.,Villanueva G.L., R.E. Novak, T.Hewagama, B.P.Bonev, M.A. DiSanti, A.M.Mandell, M.D.Smith, Science 323, 1041,(2009). [5] Geminale A., V.Formisano, M. Giuranna, Planet.Space Sci. 56, 1190, (2008). [6] Bar-Nun A., Dimitrov V. ,Icarus, 188,543, (2007). [7] Chassefiere E., Icarus, (2009) in press. .

MULTILINE PFS-MEX METHANE OBSERVATIONS AT MARS.

V.Formisano and A. Geminale , IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it).

Abstract : Several times in the past few years PFS-MEXS methane discovery has been criticized as at the limit of PFS capabilities and because only one spectral line was reported and studied [1],[2] .

In this report, using a more updated data handling procedure (adding zeroes to the interferograms to improve line strength and location, and studying transmissivity of the atmosphere for the single lines) we aim to show that PFS-MEX (spectral resolution, 1.3 cm^{-1}) has observed at least 10 methane spectral lines. In particular we shall demonstrate that PFS has been able to measure the P1,P2,P3 lines, the Q-branch and most of the R lines when they are not fully covered by water vapour lines.

We have proceeded in the following way : first from 700 orbits we collected most of the high SNR data, so that we could compute first the orbital average, and then the total average for 89000 spectra . Then from the orbital averages data set we selected the orbits having the methane band depth at 3018 cm^{-1} larger than 1% of the continuum, obtaining an average of 27000 spectra. Finally we requested the orbital averages with the methane band depth larger than 2% of the continuum. We obtained a spectrum average of only 5200 measurements. In this way we have 3 spectra with increasing methane abundance. The methane enhancement should be seen not only in the main Q-branch line, but also in all of the other methane lines, if they are not mixed with other lines (like water vapour lines, numerous in the spectral region explored).

We study the 3 spectra in the range from 2970 cm^{-1} to 3150 cm^{-1}. The 3 spectra almost coincide in the wavenumber range above 3070 cm^{-1}. The best continuum to study their transmittance is also identified. The resulting transmittance is studied and compared to solar lines, water vapour lines and methane lines. The Q-branch of a recently discovered and discussed 628 isotopologue CO_2 band is identified at 2982 cm^{-1}[3],[4]. Some minor non identified lines are shown in the 180 cm^{-1} wavenumber range. At least 45 lines are identified as water vapour lines. Methane lines at 2979, 2989, 2999, 3018, 3029, 3038, 3049(?), 3077(?), 3087, 3097 cm^{-1} have been identified, and a small line which is generated by the small Q-branch at 3021 cm-1 . The single lines of this Q-branch are less intense by a factor up to 50 than the lines of the main Q-branch. However the density of the lines is much higher than the main Q-branch, and they are all seen by PFS as a single line, resulting in another methane line in the PFS spectrum of the order of 10% of the main Q-branch.

The best fit for the 3 spectra provides a methane mixing ratio of 15, 25 and 35 ppbv.

References:

[1]) Formisano V., S. Atreya, T.Encrenaz, N. Ignatiev, M. Giuranna Science 306, 1758 (2004).). [2] Geminale A., V.Formisano, M. Giuranna, Planet.Space Sci. 56, 1190, (2008). [3] Villanueva G.L., Mumma M.J., Novak R.E., Hewagama T., Icarus 195, 34, (2008). [4] Geminale A., V. Formisano, J. Geophys. Res., Vol 114 E,(2009) .

METHANE LIMB MEASUREMENTS WITH PFS-MEX .

V.Formisano and A. Geminale , IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it).

Abstract: A number of 94 MEX orbits have been studied, in which PFS has been operated looking at limb of Martian atmosphere. The data selected have the limb distant not more than 3000 Km, so that the IFOV of PFS is still able to resolve vertical structures in the atmosphere. The total number of spectra considered is 4114. The data have been considered separately in 5 vertical groups within 0-10 Km altitude, 10-20, 20-30, 30-40, 40-50 Km altitude. The average spectrum for each altitude was computed for each season. For each season, the distribution of the data has been statistically studied from different point of view : latitude, longitude, Ls, local time distribution, tangent distance and finally the phase function. These studies allow us to state that , apart from the latitudinal distribution, there is no special bias of the data, when we study the minor gas vertical profiles.

The spring data are distributed uniformly over the latitudinal range from -60 to +60 deg latitude.

The summer data are distributed from +10 to +60 deg latitude (only northern regions).

The autumn data are distributed over the range -60 to +10 deg latitude.

The winter data are distributed over the latitude range of -80 to +30 degrees, but most of the data are between -80 and -40 degrees.

The band depth intensity of minor gases has been studied as percentage of the continuum. We are aware that this is not an absolute measurement as the continuum depends on the aerosol density at different altitudes, but this is what we can do now, while a full synthetic spectra computation software is being developed for limb geometries.

It is important to note that for the location in altitude we have been using not the PFS-MEX optical axis geometry, but the lowest possible point from the field of view of the instrument at limb.

The data show that in northern spring methane is observed only at 30-40 Km altitude, while CO and water vapour, being observed at all altitudes, have their maximum band depth at 0-10 Km altitude , decreasing with altitude. Also the aerosols, as measured by the continuum radiance at 3 different wavenumbers (2800, 4000, and 7100 cm-1) show a strange behaviour: they have a maximum at 0-10 Km altitude, but then they have a constant radiance level for all the other altitudes up to 50 km .

For the summer season the behaviour is somewhat different (but keep in mind the latitudinal distribution): methane is observed at all altitudes, but has its maximum at 20-30 Km altitude. Water vapour and CO, on the other hand , have different values below 20 Km altitude : very high value below, and a factor 2.5 times lower above 20 Km. Above this altitude, the two gases have constant abundance with altitude as band depth percentage of the continuum. In this season the aerosols show a rather strange behaviour as they decrease with altitude up to 20 Km, but then increase dramatically, and have still a very large radiance value at 40-50 Km altitude.

For the autumn season methane is observed from 0 to 30 Km altitude, but the peak is certainly at 20-30 Km. Water vapour and CO abundance as band depth percentage of the continuum show more or less constant value with altitude, with some fluctuation. On the other hand the aerosols continuum shows, at all wavenumbers, the normal behaviour : the radiance level decreases with altitude, reaching almost noise level at 50 Km altitude.

In northern winter the maximum of methane band depth as percentage of the continuum is observed at 30-40 Km altitude, and methane is observed sporadically below that altitude. Water vapour and CO show the same behaviour as in autumn. Also the aerosols continuum resemble the behaviour of the autumn season.

Our conclusions are : there is no correlation between water vapour and methane vertical profile. Methane maximum is observed at 25-35 Km altitude, therefore confirming the suggestion of E.Chassefiere, 2009 [1]. In spring and summer the aerosols continuum extends well above the 50 Km altitude.

References: [1] Chassefiere E., Icarus, (2009) in press. .

MAPPING METHANE IN MARTIAN ATMOSPHERE

A.Geminale and V. Formisano , IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it).

Abstract: After almost six years in orbit around Mars measuring the IR spectrum from 8200 to 270 cm-1 (1.2 to 45 microns), we attempt in this paper to map methane in Martian atmosphere[1]. The idea is that the methane map, providing the methane distribution , may help identifying the methane source, and therefore help in identifying the mechanism producing methane. It is clear that the highest space resolution would be welcome, as , also, separate maps for each season, in order to understand the circulation and the sink of methane also. It is clear, indeed, that the global circulation and the CO_2 polar condensation in the winter, with the increase of non condensable gases, is going to complicate the interpretation of the maps produced. Furthermore the limb measurements and the Chassefiere interpretation are going to complicate furthermore the picture of methane generation and distribution, as the global circulation is distributing not only methane, but also the clathrate hydrate that bring this molecule. The lifetime of these aerosols is not well established, so most likely they will participate to water condensation and to the sublimation of the seasonal polar cap. Because of that, the best quantity to study is not the mixing ratio of methane, but the column density.
We show the spatial and seasonal distribution of methane with the limitation that we cannot study the local polar winter regions which are almost completely absent due to poor spacecraft coverage. South of -70 deg latitude the presence of CO_2 ice prevents the evaluation of the methane abundance.
the northern remnant polar cap is the real source of methane, but the interpretation of the maps need to take into account the global atmospheric circulation (CO_2 condensation) and the suggestion by E.Chassefiere [2]that what is really transported around is not just methane, but aerosols of clatrate hydrate containing methane.
Equatorward of +-60 deg latitude the region indicated by Mumma et al 2009 [3] and by Formisano et al 2004 [1] (E-longitudes 50-150 deg) shows an enrichment of methane.

References [1]. Formisano V., S.Atreya, T.Encrenaz, N. Ignatiev, M. Giuranna Science 306, 1758 (2004). [2]. Chassefiere E., Icarus, (2009) in press.[3] Mumma M.J.,Villanueva G.L., R.E. Novak, T.Hewagama, B.P.Bonev, M.A. DiSanti, A.M.Mandell, M.D.Smith, Science 323, 1041,(2009). .

SPATIAL DISTRIBUTION AND TEMPORAL EVOLUTION OF METHANE IN THE MARTIAN ATMOSPHERE.

S. Fonti[1], G. A. Marzo[2] , [1]Department of Physics, Universita' del Salento, via Arnesano – C.P. 193, 73100 Lecce, Italy, (sergio.fonti@le.infn.it), [2]NASA Ames Research Center, Space Science and Astrobiology Division, MS 245-3, Moffett Field, CA 94035-1000, USA, (giuseppe.marzo@nasa.gov)

Introduction: After the definition of an upper limit for methane in the Martian atmosphere [1] [2], in the last few years several authors reported the detection of a very small amount of methane [3], [4], [5], [6]. Such a claim gave rise to a wide debate also because of the possible implications of such a discovery. In fact, due to the relatively short lifetime of the methane molecule in the Martian environment (about 350 years, [7]), its presence means that it is probably currently produced on the planet and hence it would be necessary to understand its production process. Suggested hypotheses are basically linked either to geothermal or biological activities [8], [9], [10], [11], [12] and, in both cases, our perspective of the planet evolution would require a major revision [13]. It is worthwhile to note that all the reported observations have been made in the spectral region of the strongest methane feature (at 3018 cm^{-1}), while the only observation made of the second strongest methane band (at 1306 cm^{-1}) yielded the upper limit given by Maguire [1]. Obviously the confidence about the presence of methane in the atmosphere of Mars will be greatly increased, if it could be detected using also measurements made in this spectral region.

Method of Analysis: We report the results of an analysis performed using the infrared spectra collected by the Thermal Emission Spectrometer (TES) on board of Mars Global Surveyor (MGS), operating in the thermal infrared [14]. In principle, its spectral resolution (6.25 or 12.5 cm^{-1}), should not be sufficient for the detection of such a narrow feature, but we have verified, through an experimental and a computational approach, that the 1306 cm^{-1} methane band is detectable by this spectrometer, averaging a few thousand spectra. We have selected about 3,000,000 TES spectra covering the region between 60º S and 60º N in latitude. Temporally they are centred at each equinox and solstice for each of the three Martian Years (MY) considered. In addition they have been collected during the warmest part of the Martian day and in nadir configuration. During MY24/25 and 26/27 MGS/TES operated mainly in the low resolution mode (12.5 cm^{-1}) while in MY25/26 in high resolution mode (6.25 cm^{-1}). This selection should provide 12 spatial/temporal slices, but the amount of usable spectra selected in Summer (Solar Longitude, Ls 90°) of MY26 was too low for considering this slice statistically reliable and we performed our analysis only on 11 slices. The number of averaged spectra is ranging between 14,000 and 43,000 for the resolution of 6.25 cm^{-1} and between 28,000 and 213,000 for 12.5 cm^{-1}. In order to deal efficiently with such a large quantity of data,

we have explored each spatial/temporal slice by means of the cluster analysis approach by Marzo et al. [15], [16], which allowed us to selectively average tens of thousand of spectra and to group them on the base of the presence of the methane feature at 1306 cm^{-1}.

Results: The methane abundances for each temporal slice have been evaluated, taking into account both the number of spectra grouped into the cluster associated with the methane band and the depth of such band in the corresponding average spectrum. A quantitative comparison between our findings and the results of other authors [3], [4], [5], [6] reveals a strong consistency, even if the temporal and the spatial scales are quite different. In addition, due to the full spatial coverage of Mars, provided by TES over a time span longer than three MY, we have been able to trace with good accuracy the spatial distribution and the temporal evolution of methane in the Martian atmosphere. The spatial distribution of methane is far from uniform with some regions of higher concentration and, at the same time, locations where the concentration of methane is very low, if not zero. In particular, there are three broad regions where the methane amount is systematically higher: Tharsis, Arabia Terrae, and Elysium. On the other hand, the temporal evolution of the methane abundance, shows large variations not only in the global amount but also in the spatial distribution. Such variations seem to follow a seasonal cycle and are different from one year to the other. The main issue is that the observed annual cycle suggests a methane lifetime of ~0.6 years [6], much shorter than previously suggested based on photochemical processes (~350 years) [4], [7], posing questions not only concerning the possible methane sources but also about its sinks.

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ABSOLUTE MEASUREMENTS OF METHANE ON MARS. M. J. Mumma[1], G. L. Villanueva[1], and R. E. Novak[2], [1]NASA – Goddard Space Flight Center (Solar System Exploration Division, Mailstop 690.3, Greenbelt, MD, 20771, USA), [2]Iona College (New Rochelle, NY, 10801, USA).

michael.j.mumma@nasa.gov, geronimo.l.villanueva@nasa.gov, rnovak@iona.edu

Introduction: The presence of abundant methane in Earth's atmosphere (~1.6 parts per million) requires sources other than atmospheric chemistry. Living systems produce more than 90% of Earth's atmospheric methane; the balance is of geochemical origin. On Mars, methane has been sought for nearly 40 years because of its potential biological significance, but it was detected only recently [1-5]. Its distribution on the planet is found to be patchy and to vary with time [1,2,4,5], suggesting that methane is released recently from the subsurface in localized areas, and is then rapidly destroyed [1,6].

Before 2000, searchers obtained sensitive upper limits for methane by averaging over much of Mars' dayside hemisphere, using data acquired by Mars-orbiting spacecraft (*Mariner 9*) and Earth-based observatories (Kitt Peak National Observatory, Canada-France-Hawaii Telescope, *Infrared Space Observatory*). These negative findings suggested that methane should be searched at higher spatial resolution since the local abundance could be significantly larger at active sites. Since 2001, searches for methane have emphasized spatial mapping from terrestrial observatories and from Mars orbit (*Mars Express*).

Results: The first definitive detections and spatial maps were achieved using high-dispersion infrared echelle spectrometers at three ground-based observatories (NASA's IRTF, W. M. Keck Observatory, and Gemini South). To date, we have detected four spectral lines of the CH_4 ν_3 band near 3.3 μm, along with H_2O and HDO [1,5,7]. Our observational campaign resumed in August 2009, now using CRIRES/VLT along with CSHELL/NASA-IRTF and NIRSPEC/Keck.

For a typical observation, the spectrometer's long entrance slit is held to the central meridian of Mars (Fig. 1, right) while spectra are taken sequentially in time. For each snapshot in time, spectra are acquired simultaneously at contiguous positions along the entire slit length, sampling latitudinally resolved spatial footprints on the planet (35 footprints, for the geometry shown in Fig. 1). Successive longitudes are presented as the planet rotates, and the combination then permits partial mapping of the planet. Our study of methane on Mars now extends over four Mars years, sampling a wide range of seasons (L_s) with significant spatial coverage. Here, we present absolute extractions of methane for our database spanning 1999-2006.

A series of such measurements taken in Mars' Northern Summer 2003 found that methane varied significantly in abundance over the surface of Mars, and in time (Fig. 2) [1,5]. In 2005, additional active regions were found in early Southern Spring [5].

In Northern summer, methane was notably enriched over several localized areas (Fig. 2): A (East of Arabia Terra, where water vapor is also greatly enriched), B_1 (Nili Fossae), and B_2 (southeast quadrant of Syrtis Major). The combined plume contained ~19,000 metric tons of methane, and the estimated source strength ($\geq$ 0.6 kilogram per second) was comparable to that of the massive hydrocarbon seep at Coal Oil Point in Santa Barbara, California. By vernal equinox about one-half the released methane had been lost. When averaged over latitude and season, spectral data from *Mars Express* also imply an enhancement in methane in this longitude range [4].

Unusual enrichments of hydrated minerals (phyllosilicates) were identified in Nili Fossae from Mars Express, and from the Mars Reconnaissance Orbiter (Fig. 2). The observed morphology and mineralogy of this region suggests that these bedrock outcrops, might be connecting with reservoirs of buried material rich in volatile species. The characteristic arcuate ridges in the southeast quadrant of Syrtis Major were interpreted as consistent with catastrophic collapse of that quadrant, perhaps from interaction with a volatile-rich substrate. This could provide conduits connecting the substrate with the atmosphere.

The most compelling results from these searches are: 1) the unambiguous detection of multiple spectral lines of methane, 2) Evidence for spatial variations that imply active release in discrete regions, and 3) Evidence for seasonal variations that imply a CH_4 lifetime of months rather than the 300-plus years implied by photochemistry. The short lifetime may be the result of reaction with strong oxidants such as peroxides located in the soil and/or on airborne dust grains [1,6,8].

The possible origins of Mars methane will be discussed in the context of geologic and biologic terrestrial analogues. Mars-analogue sites on Earth range from sub-permafrost zones that might be accessed seasonally at scarp faces, to tundra sites where its release from the near-surface photic zone is activated thermally. Key measurements needed to test its origin on Mars (biotic vs. abiotic) include fractionation (hydrogen, carbon) among isotopologues, abundance ratios of methane homologues (C_nH_{2n+2}), and tests of other possible biomarker gases (e.g., H_2S, N_2O, NH_3).

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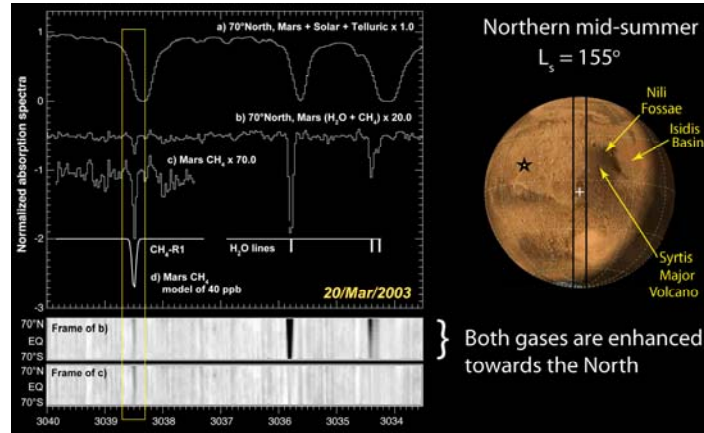

Figure 1. Right. Mars' aspect in March 2003; sub-solar (K) and sub-Earth (+) points are marked. The spectrometer entrance slit (CSHELL/IRTF) is shown to scale (vertical lines). Spectra were acquired simultaneously for 35 spatial footprints along the slit. **Left.** The spectrum at 70° N latitude (top). (b, c) Spectral signatures of Mars methane (CH_4) and water (H_2O) after subtraction of terrestrial and solar signatures. Spectral lines of water (three lines) and methane (one line) are strongest in the northern hemisphere (frame of 'b'). The latitudinal distribution of methane alone appears after subtracting a synthetic model of H_2O (frame of 'c').
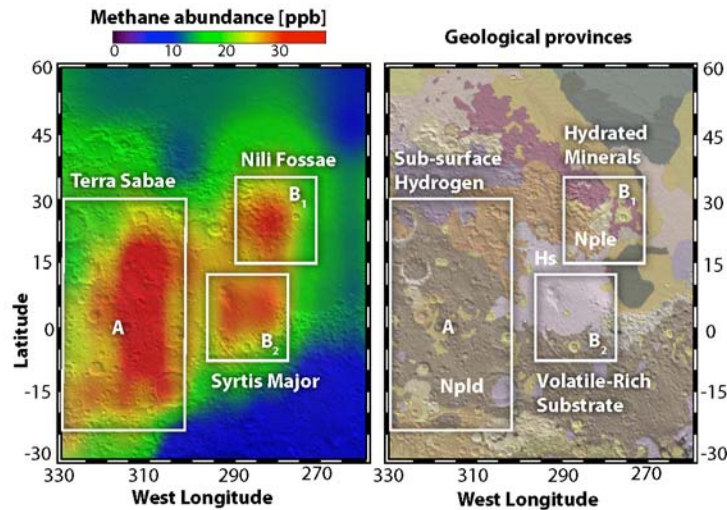
Figure 2. Regions where methane appears notably localized in Northern Summer (A, B_1, B_2), and their relationship to mineralogical and geo-morphological domains. **Left.** Observations of methane near the Syrtis Major volcanic district. Region A (Terra Sabae) is rich in sub-surface hydrogen, B_1 (Nili Fossae) displays minerals that formed in water, and B_2 (southeast quadrant of Syrtis Major shield volcano) overlaps a region that appears to have collapsed. **Right.** Geologic map (Greeley and Guest) superimposed on MOLA topographic shaded-relief. Distinct terrain types are coded by color. The most ancient terrain [dissected (Npld) and etched (Nple) plateau material] is Noachian in age (~3.6 - 4.5 billion years old, an era when Mars was wet), and is overlain by volcanic deposits of Hesperian age (light grey) from Syrtis Major (Hs, ~3.1 - 3.6 billion yrs old). After [1].

METHANE AND WATER ON MARS: MAPS OF ACTIVE REGIONS AND THEIR SEASONAL VARIABILITY.

G. L. Villanueva[1], M. J. Mumma[1] and R. E. Novak[2], [1]NASA – Goddard Space Flight Center (Solar System Exploration Division, Code 690, Greenbelt, MD, 20771, USA; geronimo.villanueva@nasa.gov), [2]Iona College (New Rochelle, NY, 10801, USA).

Introduction: We have detected methane on Mars, and measured it simultaneously with water using powerful ground-based telescopes [1, 2]. Its presence in such a strongly oxidized atmosphere (CO_2: 95.3%) requires recent release; the ultimate origin of this methane is uncertain, but it could either be abiotic or biotic. On Earth, methane is produced primarily by biology, with a small fraction produced by abiotic means.

There is ample evidence that ancient Mars was wet and likely hosted habitable conditions [e.g., 3]. Moreover, the presence of extensive volcanism probably gave rise to widespread hydrothermal activity and the formation of rich aqueous subsurface reservoirs. Methane produced by living organisms or by geological processes (e.g., serpentinization) at that time could have been incorporated into hydrates. If such processes remain active on Mars below the permafrost, the byproduct gases (i.e. CH_4 and H_2S) may be trapped as hydrates at the base of a thickening cryosphere.

Sources and Sinks: The sources and sinks of hydrogen-bearing species (e.g., H_2O and CH_4) on Mars are still poorly known. In particular, the roles of the regolith and the sub-surface hydrogen reservoirs in the Martian water cycle have been broadly studied, but have not been conclusively quantified. If water is being released from the sub-surface or shares a common source with other H-bearing species, we might see correlations among them. Previous searches for such correlations have been precluded because of the lack of simultaneity of the measurements and the intrinsic variability of water on Mars, which is a condensable whose total local abundance is partitioned among several competing phases controlled largely by temperature (ensuring its variability on a variety of time scales, from diurnal to seasonal to epochal).

Our Dataset: We sampled multiple spectral lines of methane and water vapor on Mars in a campaign spanning seven years (three Mars years; 1999-2006) and sampling three seasons on Mars. Data were acquired using long-slit infrared spectrometers: CSHELL (Cryogenic Echelle Spectrograph) at NASA-IRTF (Infrared Telescope Facility) and NIRSPEC (Near Infrared Spectrograph) at Keck 2. These instruments offer spatially-resolved spectra with the high spectral resolving power ($\lambda/\delta\lambda \sim$ 40,000) needed to reduce confusion among telluric, Martian, and Fraunhofer lines (in reflected solar radiation).

A great advantage of our dataset is that we co-measure methane (a non-condensable at Martian temperatures and pressures) and water vapor simultaneously in all spectral-spatial footprints, thereby eliminating observational effects (seeing, topography, temporal changes) that could arise if measured separately. This is especially valuable because water exhibits a strong diurnal cycle and our observations sample diverse local times (ranging from 9 AM to 3 PM), while the water vapor measurements by MGS/TES (Mars Global Surveyor / Thermal Emission Spectrometer) are taken at a fixed local time (~2 PM).

Since 2005, we greatly improved our data processing algorithms and increased the sensitivity of our measurements by an order of magnitude. Using these new techniques, we detected multiple lines of methane on Mars [1] and discovered two new band systems of isotopic CO_2 (at 3.3 and 3.7 μm) that can interfere with signatures of CH_4 and HDO [4, 5]. The spectral signatures of these isotopic CO_2 transitions may affect searches based on low spectral resolution methods, but they do not affect the searches reported herein.

Results: We present the spatial distributions of methane and water-vapor on Mars extracted from our seven-year spectral database, and we compare these with geological parameters. Both gases are depleted at vernal equinox but are enhanced in warm seasons (spring/summer), though often with dissimilar spatial distributions. In Northern Summer we observe a polar outburst of water but no methane, while in Southern Spring we observe release of abundant methane but little water.

Regions of methane release appear mainly over ancient terrain (Noachian/Hesperian, older than 3 billion years) known to have a rich hydration history.

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MEASUREMENT OF THE ISOTOPIC SIGNATURES OF WATER ON MARS; IMPLICATIONS FOR STUDYING METHANE.

R.E. Novak[1], M.J. Mumma[2], G.L. Villanueva[2], [1]Iona College (New Rochelle NY 10801 USA rnovak@iona.edu), [2]NASA – Goddard Space Flight Center (Solar System Exploration Division, Code 690, Greenbelt, MD, 20771).

Introduction: The recent discovery of methane on Mars [1,2,3] has led to much discussion concerning its origin [4]. On Earth, the isotopic signatures of methane [5,6] vary with the nature of its production. Specifically, the ratios among $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$ differ for biotic and abiotic origins. On Mars, measuring these ratios would provide insights into the origins of methane. Related measurements of water co-released with methane would assist in testing their chemical relationship. Since 1997, we have been measuring HDO and H_2O in Mars' atmosphere and comparing its ratio to that on the Earth [7,8,9]. We recently incorporated a line-by-line radiative transfer model (LBLRTM) [10] into our analysis resulting in improved retrievals of CH_4 and isotopologues of CO_2 and water. Here, we present results for [HDO]/[H_2O] using LBLRTM. From these results, we constructed models to determine the observational conditions needed to quantify the isotopic ratios of methane in Mars' atmosphere.
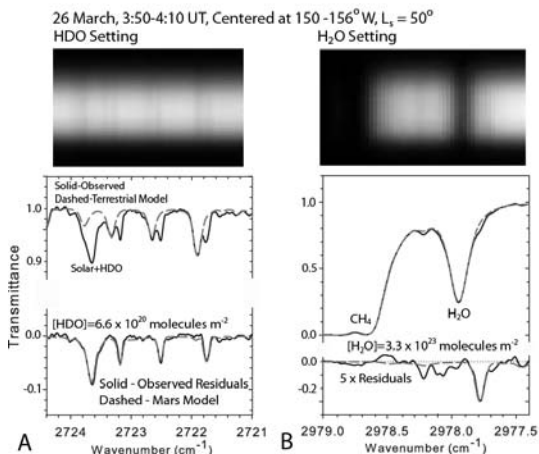

Figure 1. Spectral/Spatial images taken by CSHELL on the NASA-IRTF at HDO and H_2O settings. Three row extracts from each image provide the spectra that are centered at the sub-earth latitude (4.6^{o}N). Terrestrial atmospheric models are constructed to fit the observed spectra (upper trace); these models are subtracted from the observed spectra (lower trace). Column densities of these gases are obtained by constructing Mars atmospheric models to fit the observed residuals.

[HDO]/[H_2O]: Infrared spectrometers (such as CSHELL on NASA-IRTF and NIRSPEC on Keck II) have been used to obtain spectral/spatial images; our method for obtaining and analyzing these images has been reported [11]. Images for an HDO setting (four minutes integration time) and an H_2O setting (eight minutes) appear in Fig. 1. Three-row extracts from these images provide spectra at 0.6 arc-sec steps across Mars. With a large Doppler shift (in this case +16.5 km s^{-1}), the Mars absorptions appear adjacent to the terrestrial lines. Models that include a solar spectrum, Mars incoming and outgoing absorptions, thermal emission from Mars' surface and atmosphere, and absorptions in the Earth's atmosphere are constructed. From the best fit of the model with the observed data, vertical column densities of the water isotopologues are measured. Results across Mars appear in Fig. 2.
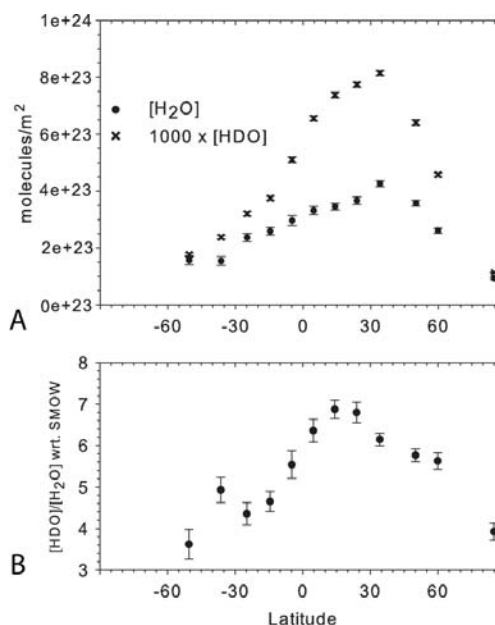

Fig. 2. A. Column densities of HDO and H_2O measured with spectral extracts at three row intervals (0.6 arc-sec). B. Ratio between HDO and H_2O compared to their ratio on earth.

Atmospheric Models for $[^{13}CH_4]/[^{12}CH_4]$: The spectral region used to retrieve [H_2O] also contains methane absorption lines. These lines are saturated in Earth's atmosphere (Fig. 1B) and a Doppler shift is needed to measure the Mars lines. Two models are presented, one from ground-based observations and the other from space-based.

Ground-based model. We first adopted the synthetic model that reproduced the terrestrial transmittan seen in Fig. 1B. A Mars model was constructed using 50 ppb of methane, 10 pr-microns of water, 95% carbon dioxide, and a surface pressure of 6 millibars. A Doppler shift of +16.5 km s^{-1} was sufficient to move the $^{12}CH_4$ line at 2978.651 cm^{-1} and the $^{13}CH_4$ line at 2978.693 cm^{-1} from the saturated portion of the terrestrial spectrum. The model spec-

tral resolution of 100,000 was able to separate these two lines (Fig. 3A); a minimum resolution of 75,000 is needed to distinguish the two lines. The modeled equivalent widths of these two lines were 0.00117 and 0.000014 cm^{-1}. The equivalent width of the observed H_2O line (Fig. 1B) was 0.0041 with a noise level of 0.0002 cm^{-1}. Based on these projection, the present IR Spectrographs, such as CSHELL/NASA-IRTF, can detect $^{12}CH_4$ but the detection of this line of $^{13}CH_4$ is not possible with its maximum resolution of ~40,000. CRIRES/VLT [12] features the needed resolving power, but the lower altitude increases terrestrial extinction, challenging the detection unless the local mixing ratio is larger than 50 ppb on Mars.
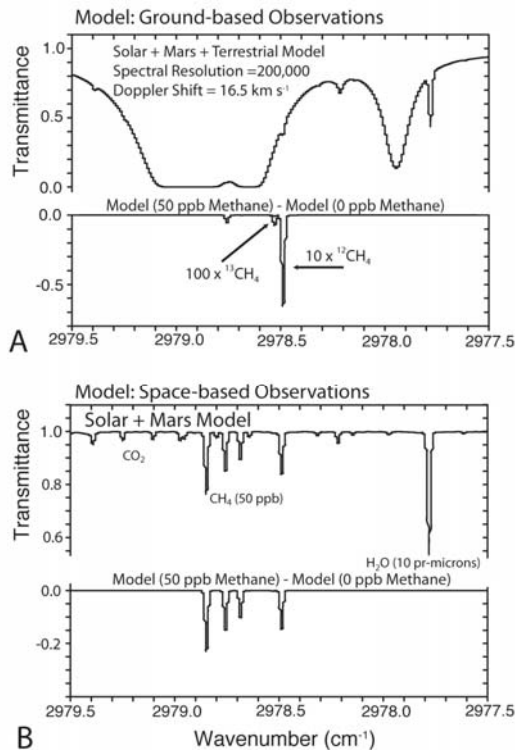

Fig. 3 Models constructed to project the measurement of methane on Mars. A. The terrestrial atmosphere filters our most of the methane absorptions on Mar. A Doppler shift of 16.5 km s^{-1} can shift the Mars absorption out of the terrestrial absorption region; a spectral resolution of at least 75,000 is needed for the isotopic lines to be separated. B. Observations from spacecraft are not affected by the terrestrial atmosphere. For the same spectral region, four separate lines of methane may be obtained.

Space-based model. A similar model was constructed (Fig. 3B) for measurements that can be made with a space-based spectrometer; for this model, there is no terrestrial extinction. The model spectrum contains solar lines and modeled Mars absorptions. In this spectral region, the Mars model

contains CO_2 lines [13], methane, and water lines. The upper trace indicates these species; the lower trace shows only the methane components. Since the Mars absorptions are not filtered out by the terrestrial atmosphere, the equivalent width (sum of the four lines) of $^{12}CH_4$ is 0.258 cm^{-1}; for $^{13}CH_4$, it is 0.0039 cm^{-1}. If the space-based spectrometer has a wider spectral grasp, sampling of the two isotopologues can be done with multiple absorption lines.

Measuring the $^{12}CH_3D$ isotopologue can also assist in determining the source of methane [5,6], but its measurement presents difficulties. $^{13}CH_4$ in earth's atmosphere is 1.11% of the total methane; $^{12}CH_3D$ is 0.06%. To project the comparable value for Mars is difficult since the D to H ratio varies with location, local time, and season [9]. Even with a global mean enhancement of D/H ~ 4.5 SMOW on Mars, $^{12}CH_3D$ would represent only 0.28% relative to $^{12}CH_4$. The column density of $^{12}CH_3D$ would still be less than that of $^{13}CH_4$ and more difficult to retrieve. Measurement of depletions relative to HDO/H_2O or cosmic $^{12}C/^{13}C$ would require even higher sensitivity, and will likely require *in situ* sampling.

Conclusion: Methane has been measured with both ground-based and space-based systems, but these systems cannot measure the ratio among its isotopologues because of their spectral resolution and signal to noise ratio. The new infrared spectrograph (CRIRES on VLT [12]) has the resolution to separate the spectral lines; with similar resolving power but higher altitude the coming cross-dispersed iSHELL/NASA-IRTF will provide improved prospects for their detection. Plans for new space-based spectrometers to measure isotopologues of methane must address considerations of spectral resolution and detectability.

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HIGH SPECTRAL RESOLUTION HETERODYNE SPECTROSCOPY OF METHANE AT 7.8 µm.

G. Sonnabend, D. Stupar, M. Sornig, P. Kroetz, I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, samstag@ph1.uni-koeln.de

Introduction: The detection of methane (CH_4) in the Martian atmosphere has been claimed by various groups since 2003 [1,2] but only recently its presence has been undoubtedly established by Mumma et al. [3] who found strong variation of methane with season, latitude and longitude at a mixing ratio of up to 40 ppb in late Northern summer. However, the question of the origin of the observed amounts of CH_4 is still open.

Ultra-high resolution spectroscopy at infrared wavelength has proven to be a powerful tool to study planetary atmospheres as many physical parameters of such atmospheres like pressure, temperature, composition or dynamics can be studied [4]. A spectral resolution of better than 10^6 allows one to fully resolve profiles of single molecular features. This is a strong advantage as the analysis of low resolution data in general requires more information about the state of the studied atmospheres which has to be provided from additional observations or models. High-resolution heterodyne spectroscopy at the strong methane band at 7.8 µm can lead to new insights to the vertical mixing ratio profile and can provide further independent prove of the existence and more detailed data on the abundance and distribution of methane in the atmosphere of Mars.

Instrumentation:

A spectral resolution of better than 10^6 at infrared wavelength can only be achieved by heterodyne techniques. Only two instruments worldwide are using this method for astronomical observations: NASA GSFC's HIPWAC (Heterodyne Instrument for Planetary Winds And Composition) and THIS (Tuneable Heterodyne Infrared Spectrometer). The latter was designed and build by our group at University of Cologne. THIS is the only astronomical receiver making use of newly developed tuneable quantum-cascade lasers (QCLs) as local oscillators (LOs) allowing us to target the whole mid-IR from 7 to 14 µm wavelength [5]. In every heterodyne instrument the broadband radiation to be analyzed is superimposed to a monomode LO and focused to a fast detector. THIS is presently equipped with QCL LOs from 7.8 to 13.6 µm. As a mixer we use a mercury-cadmium-telluride (MCT) photovoltaic detector with a quantum efficiency up to 80%. The frequency analysis is done by a 6000 channel acousto-optical spectrometer (AOS) with a total bandwidth of 3 GHz.

Planned Methane Observations:

Over the course of the next few years we plan to conduct methane observations in the strongest methane band at 7.8 µm. Those observations can only be performed from the ground at favorable radial velocity between Mars and Earth due to the strong absorption by telluric methane. The detection limit for these observations is expected to be < 10 ppb for one night of observation. A simulated
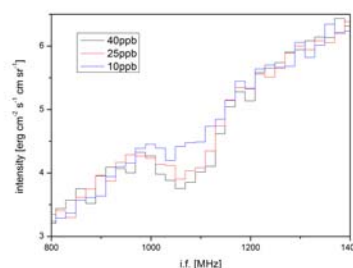

Fig 1:
Simulated spectrum of methane calculated using a full radiative transfer model. Spectra are calculated for three different volume mixing ratios of methane of 10, 25 and 40 ppb. The simulated noise represents one hour of integration time at the instrument's sensitivity at 7.8 µm which was established during a test observation in 2008.

spectrum is shown in fig. 1. In particular, we will gain some information on the vertical distribution of methane which can be extracted from fully resolved lineshapes if the signal-to-noise ratio is sufficient.

Additional Observations:

Besides information on the vertical distribution of methane, observations of other molecules related to the methane problem will provide additional clues. One of this molecules is SO_2 which is strongly connected to volcanic activities on Earth. In the case of SO_2 an upper global limit for the Martian atmosphere of 1 ppb has been established recently by Krasnopolsky [6]. His observations however did neither cover the season of maximum methane detection nor the geographical distribution. SO_2 can be observed in the infrared wavelength regime in the 8.6 µm band.

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MAPPING ICE DEPOSITS ON MARS THROUGH SUBSURFACE RADAR SOUNDING. R. Orosei[1],
G. Picardi[2], J. J. Plaut[3], R. Seu[2], R. J. Phillips[4] and the MARSIS and SHARAD teams, [1]Istituto di Fisica dello Spazio Interplanetario, Istituto Nazionale di Astrofisica, 00133 Rome, Italy (roberto.orosei@ifsi-roma.inaf.it), [2]Dipartimento INFOCOM, Università di Roma "La Sapienza", 00184 Rome, Italy, [3]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, [4]Southwest Research Institute, Boulder, CO 80301.

Introduction: the orbiting radar sounders MARSIS and SHARAD have acquired data over the surface of Mars, detecting surface deposits of ice. MARSIS [1] and SHARAD [2] are synthetic-aperture, orbital sounding radars, carried respectively by ESA'a Mars Express and NASA's Mars Reconnaissance Orbiter. They work by transmitting a low-frequency radar pulse that is capable of penetrating below the surface, and is reflected by any dielectric discontinuity present in the subsurface. Whereas MARSIS is optimized for deep penetration, having detected echoes down to a depth of 3.7 km over the South Polar Layered Deposits [3], SHARAD is capable of a tenfold-finer vertical resolution, namely 15 m or less, depending on the dielectric constant of the material being sounded. MARSIS is capable of transmitting at four different bands between 1.3 MHz and 5.5 MHz, with a 1 MHz bandwidth. SHARAD operates at a central frequency of 20 MHz transmitting a 10 MHz bandwidth.

MARSIS and SHARAD data: MARSIS has been operating around Mars since July 2005, acquiring several hundred thousands echoes over a large portion of the planet. Observations are affected by the ionosphere, which in turn is controlled by solar radiation. Thus, data acquisition using the lowest, most penetrating frequencies is possible only on the night side of the planet. The largest gap in data coverage is constituted by the northern polar layered deposits, where a combination of late antenna deployment and orbital evolution prevented observations during night time. SHARAD has accumulated more than 1 Tb of data since its start of activities in late 2006. Because of its higher resolution, coverage is achieved much more slowly than through MARSIS. Observations for SHARAD are concentrated over specific areas designated as science targets by the instrument team, and there are vast stretches of Mars where no data have been acquired. Both MARSIS and SHARAD transmit through dipoles, which have negligible directivity, with the consequence that the radar pulse illuminates the entire surface beneath the spacecraft and not only the near-nadir portion from which subsurface echoes are expected. The electromagnetic wave can then be scattered by any roughness of the surface. If the surface of Mars is not smooth at the wavelength scale, i.e. if the r.m.s. of topographic heights is greater than a fraction of the wavelength, then part of the incident radiation will be scattered in directions different from the specular one. Thus, areas of the surface that are not directly beneath the radar can scatter part of the incident radiation back towards it, and produce surface echoes that will reach the radar after the echo coming from nadir, which can mask, or be mistaken for, subsurface echoes. This surface backscattering from off-nadir directions is called "clutter", and constitutes the main problem in the identification of subsurface structures.

Results: Both MARSIS [3] and SHARAD [4] have repeatedly observed the Martian polar layered deposits, the finely stratified materials whose stratigraphy is likely related with the climate history of the planet. It was found that the PLD's are quite transparent to radar waves, implying a very ice-rich composition with only a few percent of more absorbing material, such as dust. Multiple reflections occur within both the Northern and Southern PLD's, likely caused by vertical variations of dust content. These echoes, when followed along the ground track of the spacecraft, outline a layered structure which can be connected with lateral exposures of the stratigraphy seen in images [5]. SHARAD also found ice deposits outside the polar terrains. In Deuteronilus Mensae, in the mid-northern latitudes of Mars, radar sounding data indicate that lobate debris aprons are composed predominantly of water ice [6]. Large deposits of ice, in the form of debris-covered glaciers, have also been found in eastern Hellas [7]. These glaciers likely formed in a climate different from the current one. In another site suspected of harboring water ice in western Elysium Planitia, also known as the "frozen sea" [8], subsurface layers have been detected in radar data, but their observed dielectric properties are not consistent with the presence of water ice [9].

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MORPHOLOGY AND MINERALOGY OF METHANE SOURCE REGIONS.

J. J. Wray[1] and B. L. Ehlmann[2], [1]Department of Astronomy, Cornell University, Ithaca, NY, USA 14853 (jwray@astro.cornell.edu), [2]Dept. of Geological Sciences, Brown University, Providence, RI, USA 02912.

Introduction: One of the most important results from recent searches for methane in the Martian atmosphere is the presence of spatially localized source regions [1–3]. These imply a connection between the methane release mechanism and local or regional-scale geology (surface or subsurface). Diverse remote sensing datasets, including imaging and spectroscopy, can thus be used to determine what distinguishes the methane source regions geologically, which should in turn constrain the mode(s) of methane production and/or release.

The methane source regions reported by [3] were noted to be locations with high subsurface volatile contents inferred from morphologic, mineralogic, and chemical data. We discuss further some morphologic and mineralogic aspects of source regions, focusing on Nili Fossae and the southern highlands.

Morphology: The methane source region around Nili Fossae is near one of the best exposures of Noachian crust on Mars [4]. The fossae themselves are fractures 10s of km wide and 100s of km long, but many smaller-scale fractures are also present (Fig. 1, top). Some fracture walls stand in positive relief (Fig. 1, middle), suggesting mineralization or cementation by subsurface fluids flowing through the fractures [4]. Additionally, surface fluvial erosion (seen in many Noachian-aged terrains) is evidenced by sinuous channels, depositional fans, and a crater that may have hosted a long-lived lake [5–7].

The deepest bedrock exposures show megabreccia (Fig. 1, bottom), i.e. diverse, randomly oriented blocks up to 100s of meters wide cemented into bedrock [8]. Some breccia blocks are layered [4], and there is evidence for cross-bedding, faulting, and folding of these layers, attesting to a complex history of sedimentation and tectonics predating the disruptive event(s)—probably impact—that formed the megabreccia.

Methane sources in the southern highlands, specifically in Terra Sirenum and western Thaumasia, were reported by [9]. These regions are cut by vast graben systems radial to Tharsis (Memnonia, Sirenum, Icaria, and Claritas Fossae), unique to this part of the highlands. The broad morphology of Thaumasia has been interpreted as a gravity-driven "megaslide" facilitated by abundant hydrated salts and/or ice in the subsurface [10].

Terra Sirenum hosts a dense concentration of gullies, which has been interpreted as evidence for a regional aquifer [11]. Several of these gully systems are presently active [12]. While the origin(s) of gullies remain debatable [e.g., 13], there is morphologic evidence that at least some gullies in Terra Sirenum

may have been carved by emerging groundwater [14]. In addition, global hydrologic models predict enhanced Late Noachian/Early Hesperian groundwater upwelling in Sirenum relative to the rest of the southern highlands [15], suggesting a long history of subsurface water in the region despite its relative paucity of surface valley networks [16].
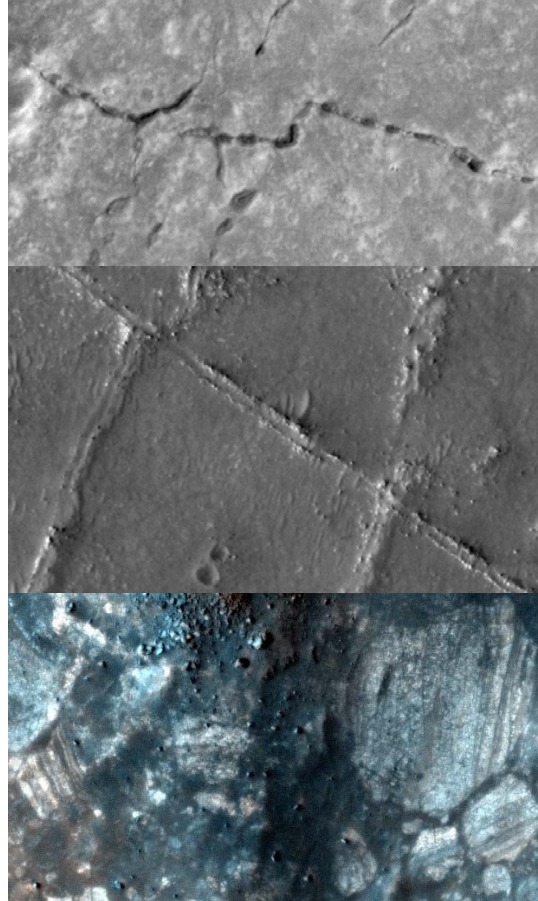
Figure 1. Surface morphology of Nili Fossae. Top: Fractures and pits (HiRISE PSP_008110_1990). Middle: Cemented fractures in inverted relief (PSP_002743_1985). Bottom: Megabreccia with internally layered blocks (PSP_006923_1995). All panels ~160 meters wide.

Mineralogy: The Nili Fossae region has the largest exposure of olivine on the Martian surface [e.g., 17] and a stunning diversity of hydrated silicates and other secondary minerals [18]. The olivine has been variably interpreted as Isidis basin impact melt [19] or early-stage lava erupted from Syrtis Major [20]. Olivine has been partially altered (Fig. 2) to form Mg-carbonate and Mg-rich serpentine [18,21,22]. Stratigraphic relations constrain the age of carbonate and serpentine-bearing rocks to ~3.9 Ga [4]. Serpentinization could have occurred more re-

cently in these ancient rocks, but the persistence of unaltered olivine throughout the region suggests minimal post-Noachian water-rock interaction. However, widespread Fe/Mg-smectite clays as well as chlorite, prehnite, mica, opal and zeolites suggest diverse alteration conditions during the Noachian [18]. Prehnite in particular indicates low temperature (200–350°C) hydrothermal conditions similar to those invoked by [23] for crustal methane formation.

Western Thaumasia is one of the very few other locations on Mars where serpentine has been identified to date [22]. To the west, Terra Sirenum hosts widespread deposits of phyllosilicates and chlorides on the intercrater plains [24,25], as well as sulfates within certain craters that may have precipitated from ancient groundwater-fed lakes [26,27].
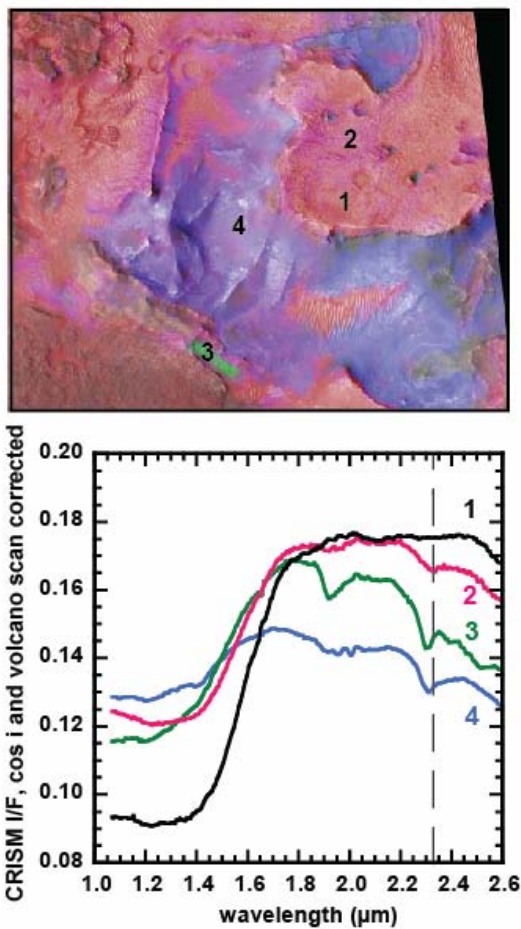

Figure 2. Alteration at Nili Fossae, figure from [18]. Top: HiRISE grayscale (PSP_002888_2025) colorized using CRISM data (FRT00003E12). Red indicates olivine, magenta partially altered olivine, green carbonate, and blue Fe/Mg-smectite. Scene is ~3 km across. Bottom: Spectra from numbered locations in (a); 2 is consistent with an Mg-rich phyllosilicate component, possibly serpentine.

Implications: As was recently noted by [28,29], the above observations hint at potential correlations between methane and surface age, deep fissures, subsurface water, and hydrated minerals including

serpentine, although source regions in Terra Sabaea and southeast Syrtis Major [3] do not share all of these characteristics. Serpentinization of olivine-rich rocks produces H_2, which can lead to abiotic methane production [23] and/or become an energy source for methanogenic organisms [30]. In either case a source of inorganic carbon is needed, and the spatial association of carbonate with serpentine-bearing rocks in Nili Fossae suggests that CO_2 was present in that alteration system.

The limited spatial coverage presented by [3] suggests a concentration of methane sources over the older highland terrains, with the younger plains of Isidis and Utopia to the east relatively methane-poor. Such an age dependence could indicate either ancient methane formation with delayed release, or a property of ancient rocks (e.g., mafic compositions, or high permeability due to impact damage) that facilitates modern methane formation and/or storage.

However, some of these loose correlations may be disproved once more complete global maps of methane are available, covering other regions with deep fractures, gullies, etc. From this perspective, we suggest that global coverage is the most critical objective for methane observations in the near future, followed by improving the spatial resolution of observations during the apparent peak of activity (spring/summer) in each hemisphere.

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THE SEARCH FOR METHANE GAS EMISSION FEATURES IN NILI FOSSAE, SYRTIS MAJOR, AND ISIDIS PLANITIA, MARS.

G. Komatsu[1, 2], G. G. Ori[1], M. Cardinale[1], J. M. Dohm[3], V. R. Baker[3], D. A. Vaz[4, 1], N. Namiki[2] T. Matsui[2], [1]International Research School of Planetary Sciences, Università d'Annunzio, Viale Pindaro 42, 65127 Pescara, Italy (goro@irsps.unich.it), [2]Planetary Exploration Research Center, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino-shi, Chiba 275-0016, Japan, [3]Department of Hydrology and Water Resources, University of Arizona, Tucson 85721, AZ, USA, [4]Centre for Geophysics, University of Coimbra, Av. Dr. Dias da Silva, 3000-134 Coimbra, Portugal.

Introduction: Because methane can only persist for a few hundred years in the Martian atmosphere, its recent detections [1, 2] indicate a present-day mechanism for its replenishment. It is of major importance to know the mechanism for replenishment and the nature and extent of the source (e.g., local vs. regional, and single vs. multiple). Investigations show that the gas is enriched over specific regions of the planet [1, 2]. The detected methane gas may result from (1) direct release from its place(s) of origin, (2) indirect release by the decomposition of gas hydrate, and/or (3) indirect release by exposure (removal of ice) of methane clathrate to the atmosphere [3]. On Earth, methane gas is often emitted from areas marked by gas- and gas hydrate-related landforms. Therefore, identifying such features is expected to provide clues on understanding the methane-replenishing mechanisms on Mars. Although there have been works on potential gas- and gas hydrate-related features on Mars in the past [e.g., 4, 5], relatively little attention has been paid to the roles of gases and gas hydrates on Mars to this date.

We have conducted a preliminary investigation of possible gas- and gas-hydrate-related features on Mars over methane-enriched regions using images acquired by various recent Mars missions. We focused our initial study on Nili Fossae, Syrtis Major, and Isidis Planitia, three methane-enriched regions [1, 2].
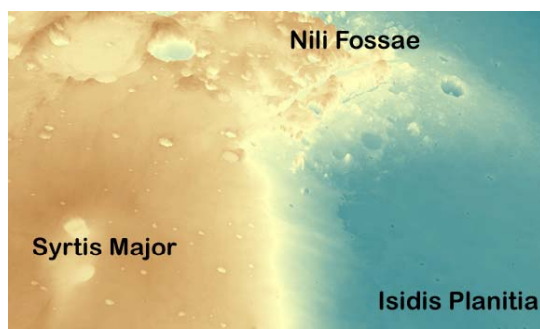

Fig. 1. Locations of the study areas. 3-d perspective view based on MOLA topography.

Preliminary results:

Nili Fossae. A system of fractures characterizes Nili Fossae, and dark-toned flows from Syrtis Major invade some of the fractures. Methane concentration is elevated over Nili Fossase, and the fractures may represent a zone of gas venting conduits where methane and other volatiles migrate from the subsurface with eventual release into the atmosphere. The recent detection of serpentinite [6] in the Nili Fossae region should be considered as a contributor to methane production, since serpentinization leads to methane production on Earth.

Syrtis Major. Syrtis Major is considered to be a volcanic field comprised of low-shield volcanoes. A number of dark-toned flows spread radially from two distinct calderas. The dark-toned flows are generally interpreted as solidified lava. Because methane emission is observed from terrestrial volcanoes, Syrtis Major may analogously be hypothesized to be a site of magma-driven gas venting.

Isidis Planitia. The Isidis basin floor is characterized by the presence of a dark-toned unit and associated, often aligned mounds. The mounds are <1 km in diameter and often have summit craters. The interpretations for the mounds include pingos, volcanoes, and mud volcanoes [7, 8], all of which may have gas emission capacity.

Conclusions: Our work highlights the need for further investigation of methane gas emission on Mars in regard to (1) the mechanism(s) of emission (e.g., serpentinization, decomposition of gas hydrates, exposure of methane clathrate to the atmosphere, or magma-driven activity, including hydrothermal activity and the role of living organism) and (2) vent(s) (landforms including fractures of Nili Fossase, calderas of Syrtis Major, mounds of Isidis Planitia, etc.), which includes extent (e.g., one or more and local vs. regional).

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SURFACE CONDITIONS FROM THERMODYNAMICS OF PHYLLOSILICATES AND IMPLICATIONS FOR THE PRESENCE OF METHANE ON EARLY MARS.

V.F. Chevrier[1], [1]W.M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, USA. vchevrie@uark.edu.

Introduction: The Mars Express OMEGA and Mars Reconnaissance Orbiter CRISM imaging spectrometers have identified phyllosilicates (Fe, Mg, Ca-smectites, kaolinite and chlorite) in Noachian aged terrains [1-3], often associated with lacustrine or fluvial deposits [4,5]. Carbonates have also been recently identified in similar areas [6]. Clay minerals usually result from long term weathering of primary minerals by liquid water at neutral to alkaline pH [7]. Their presence with carbonates [6] suggests an early environment completely different from the acidic conditions responsible for the formation of sulfate outcrops widely observed on Mars [8]. Although, previous results have shown that the dominance of smectites over carbonates indicates rather a CO_2-poor atmopshere (Fig. 1, [7]), where CO_2 could thus be replaced by other greenhouse gas such as methane.

Starting from the hypothesis that phyllosilicates are formed by liquid water induced weathering of the primary basaltic outcrops, thermodynamic models are used to study the conditions on the surface during the Noachian. Focus was placed on the effect of CO_2 partial pressure and temperature on the parageneses.
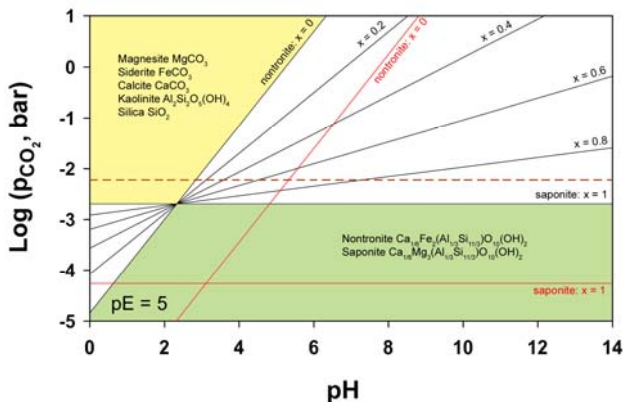

Figure 1. Equilibrium between carbonates and phyllosilicates as a function of the partial pressure of CO_2 and the pH, and for various Mg/(Mg+Fe), mol compositions. High Mg compositimons, characteristics of early Mars (as shown by the ALH84005 meteorite).

Methods: The water composition data presented in Table 1 was used as input of the models. This composition reflects possible primary solutions on Mars [9]. Al^{3+} and SiO_2 have been set up at typical terrestrial values, being generally driven by their low solubility. The Geochemical Workbench software package was used to model thermodynamic equilibria, with the *thermo.com.v8.r6+* database, which contains about 350 common silicates.

This database uses Debye–Huckel theory for ionic activities, which is perfectly accurate to describe behavior of solutions at relatively to very low concentrations.

Table 1. Concentrations and activities of dissolved species from [9] except for Al^{3+} which is estimated in this work.

Specie	Log (Activity, 10^{-3} mol l^{-1})	Concentration (mg L^{-1})
SiO_2	-4.5	60.1
Al^{3+}	-5	0.3
$Fe^{2+/3+}$	-3.1	44.7
Mg^{2+}	-3.0	24.3
Ca^{2+}	-3.3	20
K^+	-4.2	2.7
Na+	-3.1	18.4
SO_4^{2-}	-3.7	17.3
Cl$^-$	-3.2	23

Temperature effect: the effect of temperature was tested in reducing conditions which correspond to typical terrestrial hydrothermal systems. In all cases (even at high oxidation), nontronite appears only stable at low temperatures, below 150ºC (Fig. 2). At low temperatures, siderite is present only in reducing conditions and kaolinite appears only in high p_{CO_2} (Fig. 2 B). At higher temperatures, the mineralogical paragenesis is composed of diaspore, saponite and chlorite (amesite) at low p_{CO2}. At higher p_{CO2}, chlorite is replaced by serpentine (antigorite). In all cases, the excess of iron is converted into hematite. The composition in Table 1 is relatively iron-rich. Higher concentrations in magnesium, relative to iron, result in more abundant chlorite, serpentine and saponite.

Discussion: During the alteration process of olivine, two main processes occur: first the olivine is converted into serpentine:

$6 Fe_2SiO_4 + 7 H_2O = 3 Fe_3Si_2O_5(OH)_4 + Fe_3O_4 + H_2$
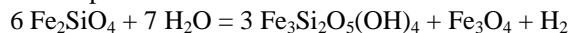
Since this olivine is iron-rich (fayalite pole), H_2 is produced as a result of iron oxidation and reduction of water. The reacrion produces also greenalite which can be enriched in Fe^{3+}, resulting in more iron oxidized and more H_2 produced. The H_2 produced can react with CO_2 to form methane [10,11]:

$4 H_2 + CO_2 = CH_4 + 2 H_2O$
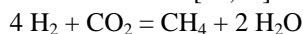
Alternatively, for magnesian poles, the alteration of the forsterite pole does not produce H_2:

$2 Mg_2SiO_4 + 3 H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$
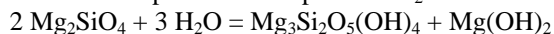
Thus methane is only an ouotcome of iron oxidation. Nevertheless, a processus called carbonation occurs when serpentine formed at high temperature reacts with CO_2 to form carbonate tmagnesite and talc [12]:

$2\ Mg_3Si_2O_5(OH)_4 + 3\ CO_2 = Mg_3Si_4O_{10}(OH)_2 + 3\ MgCO_3 + 3\ H_2O$
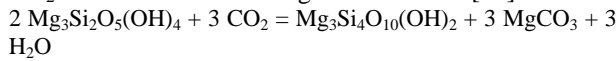
This reaction can occur when the temperature decreases (Fig. 3) or if the CO_2 pressure increases. Therefore, this reaction represents an alternative CO_2 sink to methane production. The similar reaction is also possible for iron phases, resulting in minnesotaite (iron pole of talc) formation
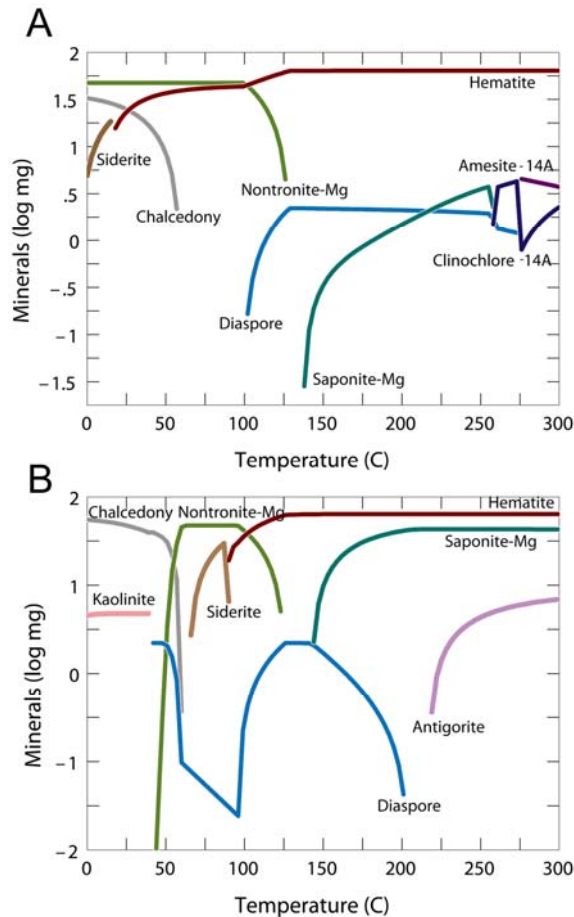
Figure 2. Evolution of the secondary paragenesis as a function of the temperature of the system in reducing conditions (pe = 0)0. (A) Low $p_{CO2} = 0.006$ bar. (B) High $p_{CO2} = 1$ bar. High temperatures favor the formation of chlorite phases at low p_{CO2}. Talc and saponite form at higher p_{CO2}.

Conclusions: These results confirm that the Noachian parageneses are controlled by the CO_2 partial pressure and temperature, rather than pH or water abundance [7]. The observation of serpentine in Nili Fossae [13] indicates hydrothermal alteration of olivine, although the presence of magnesite shows that carbonation processes

and thus reaction with CO_2 probably occurred at relatively high temperature, preventing its release in the atmopshere. Then the presence of nontronite indicates that conditions probably evolved from early hydrothermalism at the end of the emplacement of the olivine bedrock, to surface weathering and evaporation in low CO2 partial pressure (Fig. 1).

The presence of magnesite indicates that CO_2 reacted with the basement rocks and if some iron-bearing phases were present they probably got oxidized, resulting in methane formation, although no iron-rich secondary phyllosilicate (greenalite, minnesotaite) has been indentified in this region. This would however provide an ideal environment for life to appear and eevolve. On Earth, methanogen bacteria interfere in the process of carfbonation of iron phases, and facilititate the conversion to methane from H_2 and CO_2. Thus iron-rich phases would provide and better environment than just magnesium, by producing the energy source for archea.
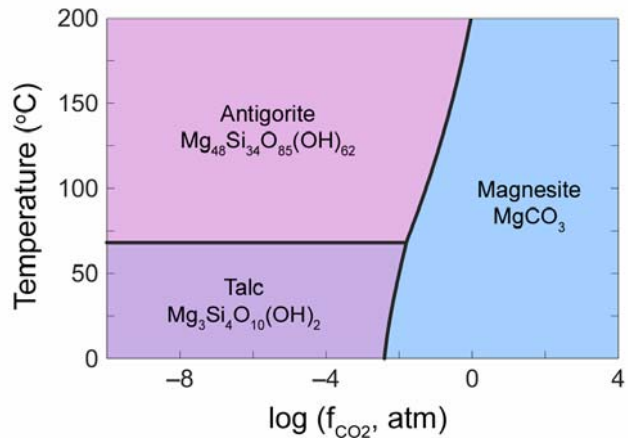
Figure 3. Equilbrium of magnesium silicates, serpentine (antigorite) and carbonates as a function of temperature and p_{CO2}. This diagram illustrates the processus of carbonations where silicates are converted into carbonates.

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LABORATORY INVESTIGATION OF THE ROLE OF HETEROGENEOUS PROCESSES IN MARTIAN METHANE VARIABILITY.

R. V. Gough[1], M. A. Tolbert[1], C. P. McKay[2], D. De Haan[3] and O. B. Toon[4], [1]Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309 (raina.gough@colorado.edu), [2]NASA Ames Research Center, Division of Space Sciences and Astrobiology, Moffett Field, CA 94035, [3]Department of Chemistry, University of San Diego, San Diego, CA 92110, [4]Laboratory for Atmospheric and Space Physics and Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO 80309.

Introduction: The cause of the spatial and temporal variability in the concentration of methane (CH_4) in the Martian atmosphere [1-3] is unknown, as the only currently known loss pathways (photolysis and gas-phase oxidation) occur over hundreds of years and should result in well-mixed CH_4 [4]. It is possible that there are currently unknown CH_4 sources and sinks with much shorter lifetimes, perhaps even less than one Martian year [2, 3, 5]. In the past, we have studied the reversible, temperature-dependent adsorption of CH_4 by JSC-Mars-1 [6], and found the process to be slow, although the importance of this temporary, seasonal sink has yet to be determined. However, ever since the Labeled Release (LR) experiment onboard Viking discovered that samples of the regolith were able to oxidize organics to CH_4, it is commonly thought that the Martian regolith contains a strong oxidizing agent. Laboratory simulations suggest that hydrogen peroxide (H_2O_2) is likely responsible for the LR results [7]. This H_2O_2 could be photochemically [8] or electrochemically [9] produced in the atmosphere and then complex with the surface soil grains. It has been frequently proposed, although not yet experimentally investigated, that this surface oxidant is destroying atmospheric CH_4. Perchlorate (ClO_4^-), another strong oxidant, was recently discovered to exist in the polar regions [10]. Although it is believed that perchlorate salts are unable to oxidize organics or CH_4 under Martian temperature conditions, to the best of our knowledge this has not been experimentally studied.

Experiments performed: We are experimentally investigating the oxidation of CH_4 by several types of possible oxidative soil analogs: titanium dioxide complexed with hydrogen peroxide ($TiO_2 \cdot H_2O_2$), a material shown to closely mimic the reactivity of the Martian soil [7], as well as magnesium perchlorate hexahydrate ($Mg(ClO_4)_2 \cdot 6H_2O$), the stable form of $Mg(ClO_4)_2$ on Mars, and JSC-Mars-1 treated with H_2O_2. The oxidation studies are performed in vials sealed with rubber septa. The "Viking mixture" of organics (a solution of glycine, alanine, formic acid, glycolic acid, and lactic acid) was also added to a series of vials for comparison. After addition of either CH_4 or the organics to the vials, a sample of the headspace was extracted at 24, 48 and 72 hr and in-jected into a gas chromatograph (GC) for quantitative analysis of CO_2.
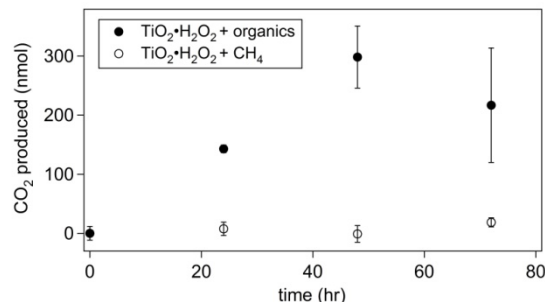
Fig 1. CO_2 produced from a 0.1 g $TiO_2 \cdot H_2O_2$ sample after the addition of either organics or CH_4 (T = 275 K).

Results: All oxidant analogs, $TiO_2 \cdot H_2O_2$ (see Fig. 1), $Mg(ClO_4)_2 \cdot 6H_2O$, and JSC-Mars-1 with H_2O_2 oxidized the organic solution to some extent; however, no reaction with CH_4 was detected. The limit of detection of the GC can be used to determine an upper limit of reactivity for heterogeneous CH_4 loss, and these kinetic limits can be applied to CH_4 loss on Mars. We will report these limits of reactivity, and the corresponding lifetimes of Martian CH_4.

Preliminary results suggest that the oxidation of CH_4 by these three oxidant analogs is slow. A recent modeling study determined that if CH_4 loss is occurring at the Martian surface, the lifetime of CH_4 must be very short, on the order of hours [5]. None of the oxidant analogs studied are capable of oxidizing CH_4 this rapidly. If surface loss is responsible for the atmospheric CH_4 variability on Mars, the chemistry occurring is yet unknown.

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METHANE AND THE MARTIAN HABITABILITY

Sushil K. Atreya[1], Paul R. Mahaffy[2], Christopher R. Webster[3], and Patrice Coll[4], [1]University of Michigan, Ann Arbor, Michigan 48109-2143 USA (atreya@umich.edu), [2]NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA, [3]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, [4]LATMOS and University of Paris VI, France

The methane of the earth's atmosphere is more than 90% biological in origin. Thus, the detection of trace quantities of methane (average 15 ppbv) in the atmosphere of Mars by the Mars Express Planetary Fourier Spectrometer [1] and ground-based telescopes [2,3] in 2003 raised the prospect of possible microbial presence on Mars, currently or in the past. However, methane could well be hydrogeochemical in origin. Irrespective of the actual *origin*, the presence of methane points to the presence of sub-surface aquifers, as *liquid* water is needed in either case. Several measurements, including carbon isotopes, chirality of organic molecules, heavy hydro-carbons, geological and geochemical context, etc. are essential to discriminate between the geological and the biological origin. The non uniform distribution of methane on Mars points to the manner in which methane is delivered to the atmosphere and how it is removed, again irrespective of the origin of methane. Delivery to the atmosphere from subsur-face *sources*,

such as hydrates, directly, or as cloud-borne clath-rates (E. Chassefiere, personal comm.), is possible. Removal of methane (and the surface organics) could be accelerated by oxidants, such as *surface*

hydrogen peroxide or hydroxyl radicals or super-oxides derived from the peroxide [4,5,6], or perchlo-rates detected previously at polar latitudes by the Phoenix lander. The resulting lifetime of methane would be shortened considerably, which would re-quire a large production rate of the gas to maintain it at the observed levels [4,6]. The Sample Analysis Suite of instruments including a Gas Chromatograph Mass Spectrometer and the Tunable Laser Spec-trometer on the 2011 Mars Science Laboratory will measure methane, $^{12}C/^{13}C$, and related trace species and isotopes, which will go a long way in under-standing the habitability of Mars (talks by P. Mahaffy, C. Webster, P. Coll). Localization of the methane vents/fumaroles to within 10-20 km will be essential in future missions to make further progress. Additional info and pdf's: www.umich.edu/~atreya

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CH$_4$ PRODUCTION ON MARS BY PHOTOLYSIS OF H$_2$O IN THE PRESENCE OF CO.

Akiva Bar-Nun and Vasili Dimitrov, Department of Geophysics and Planetary Sciences, Tel-Aviv University, Tel-Aviv, 69978, Israel. E-mail: akivab@post.tau.ac.il

We have shown experimentally that photolysis of H$_2$O in presence of CO produces CH$_4$ [1].

H atoms are produced by water photolysis and by reaction of OH with CO to form CO$_2$.

(1) $\quad$ H$_2$O $\xrightarrow{\text{UV}}$ H + OH

(2) $\quad$ OH + CO $\longrightarrow$ H + CO$_2$
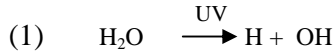
Most of the H atoms recombine to form H$_2$ and the major products of the reaction are H$_2$ and CO$_2$.

However, some of the H atoms attach to CO and form, consecutively, H$_2$CO, CH$_3$OH and finally CH$_4$.

Thermodynamic equilibrium calculations (although the Martian atmosphere is not at equilibrium), show that CH$_4$ and its precursors should be formed under Martian atmospheric conditions [2, 3].

Our proposal can be easily tested by correlating the observations of CH$_4$ and H$_2$O on Mars.

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Methanogenesis in terrestrial permafrost: a model for methane sources on Mars? D. Wagner[1] and D. Möhlmann[2], [1]Alfred Wegener Institute for Polar and Marine Research, Telegrafenberg A45, 14473 Potsdam, Germany, email: Dirk.Wagner@awi.de, [2]DLR Institute for Planetary Research, Rutherfordstr. 2, 12489 Berlin, Germany, email: Dirk.Moehlman@dlr.de.

Introduction: Apart from the global relevance of permafrost as a large carbon reservoir, this extreme environment is also of particular interest to astrobiological research, as an analogue for extraterrestrial permafrost habitats, which are a common occurrence in our solar system. Particularly, the observation of methane in the Martian atmosphere by the current mission of the European Space Agency, Mars Express [1] has stimulated the debate over possible microbial life on Mars. Recently, it has been shown that methanogenic archaea isolated from Siberian permafrost environments are more tolerant to environmental stress and simulated thermo-physical Martian conditions than methanogens from temperate ecosystems. Microorganisms from terrestrial permafrost are valuable model organisms in our effort to investigate the possibility of microbial life in extraterrestrial permafrost ecosystems.

Methanogenic Archaea: Responsible for the biogenic methane production (methanogenesis) on Earth is a small group of microorganisms called methanogenic archaea [2]. Methanogenic archaea, which are one of the initial organisms on Earth, are widespread in nature and highly abundant in extreme environments tolerating low/high temperatures (permafrost, hot springs), extreme salinity (saltern ponds) and low/high pH (solfataras, soda lakes). Although, they are regarded as strictly anaerobic organisms without the ability to form spores or other resting stages, they are found in millions of years old permafrost sediments [3]. They are characterized by lithoauthotrophic growth gaining energy by the oxidation of hydrogen, and carbon dioxide can be used as the only carbon source.

Stress Tolerance of Methanogens from Siberian Permafrost: Methane-forming microorganisms were isolated from Siberian permafrost-affected soils and their survivability was studied under extreme environmental conditions. The organism *Methanosarcina* SMA-21 was proven to be particularly resistant. It can survive extremely low temperatures down to minus 79°C and long freezing periods of up to 2 years with little harm. It is also resistant to high salt concentrations, long periods of starvation (up to three months), intensive UV (UV-C 700 J m^{-2}) and ionizing radiation (6-12 kGy) and can endure desiccation up to 25 days. Methane-forming reference organisms from non-permafrost habitats, however, are very sensitive and died during these stress experiments [4].

In a three-week simulation, the microorganisms were exposed to present climatic conditions on Mars. The daily temperature amplitude fluctuated between minus 75°C and plus 20°C, and the amount of available water varied between extremely dry and humid (a$_w$ 0.1-0.9). *Methanosarcina* SMA-21 survived without any difficulty and showed a similarly high methane production before and after the experiment. The reference organisms, on the other hand, were no longer able to produce methane after the simulation [5].

Preliminary Biogenic Martian Methane Balance: The typical order of magnitude of the production rate of methane by terrestrial methanogenic archaea in soil of an average temperature of about -6°C is about 0.14 nmol h^{-1} g^{-1}, where the mass (measured in g) is that of the soil [6]. This corresponds to about 4 x 10^{-6} kg h^{-1} m^{-3}, if a mean soil mass density of 2 g cm^{-3} is taken. Obviously, a local volume of the upper martian surface of about 1.3 x 10^7 m^3 (corresponding to an only 235 m sized cubus) of soil with terrestrial methanogenic archaea would be necessary to produce the required mars-relevant amount of methane of about 34 kg methane per hour under terrestrial conditions. With respect to Mars, the following conditions in the upper martian subsurface are to be taken into account:

a) The thickness of the biologically effective upper subsurface can assumed to be of the same order of magnitude as the diurnal thermal penetration depth L of the soil with mass density ρ, heat conductivity λ, heat capacity c, and duration of one day P,
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b) The duration of the biologically active period per day can be expected to be of only a few hours. Three hours will in the following be taken as an exemplary value. Furthermore, seasonal variations may bring in another factor of about ½.

c) According to the Arrhenius equation, the reaction rate of processes with an activation energy E$_a$ decreases exponentially with temperature
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d) The reaction rate of biological processes decreases correspondingly. Processes at T around about 240 K and 250 K are therefore

slower by about one to two orders of magnitude than those around 270 K. A factor 1/30 will be taken for numerical estimates.

The above given estimated values give a factor of about 2×10^{-4} ($0.1 \times 1/8 \times \frac{1}{2} \times 1/30$) with respect to the possible surface area above a hypothetical biologically active methanogenic subsurface volume. This hypothetical total surface area of seasonally and diurnally variable biologically active methanogenic subsurface parts on Mars is in the range of 10^{10}-10^{11} m^2, corresponding to a few 100-km sized or to possibly multiple 10-km sized surface spots above hypothetical biologically methanogenic shallow subsurface parts.

Conclusion: In conclusion, our studies show that Methanogenic archaea from Siberian permafrost environments are well adapted to these extreme environmental conditions, and could even survive under Martian conditions. The preliminary calculation of a potential biogenic methane source on Mars, which are based on measured methane concentrations in the martian atmosphere and on production rates of terrestrial methanogenic archaea show that a hypothetical biologically methanogenic subsurface source, similar to methanogenic archaea in terrestrial permafrost, could be the cause of the observed quantities and patterns of methane on Mars.

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Methane Sources and Sinks: The Geobiology of the Arctic versus Mars. T.C. Onstott[1], S. Tronick[1], J. Fleming[1], Y. Chen[1], L. Pratt[2], A. Johnson[3], L. Whyte[4], K. Lehmann[5], P. Mahaffy[6], J. Burris[6], V. Holmes[6], N. Kashem[6], I. Los ten Kate[6] and J. Kessler[7], [1]Dept. of Geosciences, Princeton University, Princeton, NJ, USA 08544 (tullis@princeton.edu), [2]Department of Geological Sciences, Indiana University, Bloomington IN, USA 47405, [3]Department of Molecular and Cellular Biochemistry, Indiana University, Bloomington IN, USA 47405, [4]Department of Natural Resource Sciences, McGill University, Montreal, Quebec, CA, H3A 2T5, [5]Department of Chemistry , University of Virginia, Charlottesville, VA, USA 22904-4319, [6]NASA Goddard Space Flight Center, Greenbelt, MD, USA 20771, [7]Dept. of Oceanography, Texas A&M University, College Station, TX, USA 77843-3146.

Introduction: One of the most important discoveries in planetary sciences related to Mars in this decade has been the seasonal and spatial variation in atmospheric CH_4 [1-3]. Seasonality in the CH_4 atmospheric concentration imposes severe constraints on the source generation rates as discussed by Lefévre and Forget [4]. Seasonal fluctuations in the CH_4 fluxes above arctic permafrost of Earth have recently been reported in detail [5-8] and we review these processes in further detail along with new results of microbial experiments under Martian environmental conditions and new developments regarding technologies for measuring the isotopic composition of martian atmospheric CH_4.

CH_4 Flux in Canadian Arctic: The CH_4 flux above shallow permafrost deposits in Siberia and Greenland exhibits a seasonal variation that spans at least three orders of magnitude. Some of the positive excursions are related to physical processes such as freezing [5]. Some of the variation in flux can be correlated with temperature and the varying CH_4 production rate from methanogens and consumption rate of aerobic methanotrophs [6]. Negative CH_4 flux recorded from Axel Heiberg Island in the Canadian high arctic in early spring suggest both methanogenesis and methanotrophy are present in the active layers above permafrost. The extent to which the CH_4 flux from terrestrial permafrost is constrained by kinetic or thermodynamic processes has not been fully resolved due to the paucity of measured electron donor concentrations. In sub-permafrost environments in the Canadian high arctic such measurements indicate that the high pH of water/ rock interactions can act as an energy bottleneck for methanogenesis [8].

Terrestrial Methanogens in Martian Environments: Experiments exposing methanogens from terrestrial permafrost deposits to martian environmental conditions have yielded mixed results. In some instances methanogens have proven remarkably capable of surviving short-term exposure to martian pressures and temperature fluctuations [9]. In other instances using simulated martian regolith survival of methanogens was poor, yet CH_4 production by an autotrophic methanogen could still be detected.

New Technologies for Characterizing Martian CH_4: Rivkina et al. [7] have reported $\delta^{13}C$ values of CH_4 from Siberian permafrost ranging from -64 to -100 ‰ VPDB. These results and the low CH_4/CO_2 relative abundance suggests that the isotopic composition of martian CH_4 will prove a powerful constraint on the its origin. As a result we are developing a near-IR CRDS for the accurate measurement of the $\delta^{13}C$ and δ^2H of CH_4. The current model has the potential of achieving adequate precision in both isotopes for martian CH_4 that has been concentrated by a factor of 50.

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ABIOTIC METHANOGENESIS DURING CARBONATE REDUCTION BY HYDROGEN-BEARING FLUIDS: A MECHANISM FOR MARTIAN METHANE. C. Lazar[1] and C. E. Manning[2], [1]Department of Earth and Space Sciences, University of California at Los Angeles (lazar@ess.ucla.edu)

Introduction: Water-rock interaction is often proposed as a mechanism for generating CH_4 on Mars [1,2]. However, the physical chemistry of hydrothermal methanogenesis is poorly understood. Field and experimental studies suggest that reduced C-O-H fluids do not readily achieve equilibrium, owing to the slow kinetics of CO_2 reduction to CH_4 [3]. Experimental fluids with significant CH_4 concentrations have been produced using synthetic transition metal catalysts such as pure Fe-chromite [4], or nickel-iron alloy [5]. However, recent experiments using natural magnesiochromite, common in many terrestrial ultramafic and mafic assemblages, did not produce significant CH_4 [6]. Furthermore, metamorphic awaruite (Ni_3Fe alloy) is uncommon in terrestrial rocks; its stability range is restricted to a narrow range of temperature (T) and oxygen fugacity (fO_2) during only the earliest stage of serpentinization [7]. We present preliminary experimental data for an aqueous methanogenesis process that does not involve a transition metal catalyst: the reduction of carbonate minerals by hydrogen-bearing fluids.

Methods: Equilibrium calculations at 10 kbar and 550°C suggest that, as fO_2 decreases below QFM, calcite solubility increases until portlandite ($Ca(OH)_2$) becomes the stable solid phase. The solubility increase may be explained by the combined reaction, $CaCO_3 + 4H_2 + 2H^+ = Ca^{2+} + 3H_2O + CH_4$, which is driven to the right by an increase in H_2. At low fO_2, when portlandite is stable relative to calcite, the fluid is predominantly a mixture of CH_4, H_2, and H_2O. To test whether the kinetics of this reaction are favorable for significant methanogenesis, we reacted isotopically labeled $Ca^{13}CO_3$ with pure H_2O, buffered at oxidizing and reducing fO_2 values (see below). Our experiments were performed in a piston cylinder apparatus at 550°C, 10 kbar and 15 kbar, in welded Au capsules for approximately 24 hours.

The fO_2 was internally buffered using welded Pt capsules containing the one of following assemblages: nickel-nickel oxide (NNO, ΔQFM ~ +1), awaruite-magnetite (AM, ΔQFM ~ -3 to -4), and iron-magnetite (IM, ΔQFM ~ -5). Carbonate minerals (calcite or aragonite, depending on pressure) are theoretically stable at NNO, but portlandite is stable at both AM and IM. AM was created by reacting natural awaruite (josephinite) with water, which stabilizes magnetite plus a more nickel-rich alloy. AM is not a buffer *sensu stricto*; it constrains fO_2 to range of values. In the present experiments, electron microprobe analyses of Fe in the alloy products sug-

gest that this range spans about 0.5 log fO_2 units, yet entirely within the portlandite stability region.

Methane was analyzed by piercing the sealed Au tubes inside a gas vial, extracting the contents with an airtight syringe, and injecting into a GC-MS. Methane was detected at AM (15 kbar) and at IM (10 kbar), but not at NNO (15 kbar). These results agree qualitatively with our calculations. After gas analyses, the capsules were opened to examine the solid products. Graphite was not observed. Portlandite and calcite were visible in the IM run, aragonite in NNO and AM. The occurrence of calcite and aragonite suggests that methanogenesis is not restricted to any particular $CaCO_3$ polymorph. Portlandite was not clearly visible in the 15 kbar AM-buffered run, suggesting that the rate of the reaction is somewhat dependent on hydrogen activity. In a supplementary suite of experiments not analyzed for gas content, calcite buffered at AM converted to portlandite after a few days, while calcite buffered at IM converted to portlandite in a few hours or less.

Results and discussion: Quantitative experiments will be performed in the near future in order to measure the rate of reaction, and to assess whether the fluids reach equilibrium. Regardless of whether the process leads to an equilibrium fluid, hydrogen-driven carbonate reduction appears to produce methane-bearing fluids. If hydrothermal activity in the Martian subsurface generates H_2 rich fluids, then upward percolation of these reduced fluids through carbonate-bearing strata and/or soils may generate methane. Carbonates are believed to exist – perhaps ubiquitously – on the Martian surface [9, 10], thus the limiting factor in our hypothesis is whether hydrogen generation occurs on Mars via serpentinization or some other process. Future work will be performed at lower pressures and temperatures to assess whether calcite-derived CH_4 occurs at shallow crustal depths.

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METHANE RESERVOIRS ON MARS: A STORY OF MIGRATION, GAS HYDRATES, TRAPS, AND A LONG PRODUCTION CYCLE. G. G. Ori[1, 2], G. Komatsu[1, 3], [1]International Research School of Planetary Sciences, Università d'Annunzio, Viale Pindaro 42, 65127 Pescara, Italy (ggori@irsps.unich.it), [2]Ibn Battuta Centre, Universte Cady Ayyad, Marrakech, Morocco, [3]Planetary Exploration Research Center, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino-shi, Chiba 275-0016, Japan.

The discovery of Methane in the atmosphere [1, 2] has clearly shown that the subsurface of Mars is a place with vigorous energy exchange. The fact that the methane is not evenly distributed in the atmosphere is surprising. Clearly the methane cannot be transferred from the subsurface to the atmosphere homogeneously over the planet, but several "points of transfer" appear to spread over the surface.

At this stage biogenic or abiogenic methane production should be considered as source. However, it is better to use a conservative approach until the presence of life forms is clearly detected. Then, the best source of methane is the serpentinisation of basalts in the subsurface. It has been already demonstrated that basalts in the Martian subsurface would undergo alteration producing serpentinites and, consequently, methane. In geological term, the slow production rate of methane in the Martian subsurface is compensated by the long time span available for the methane production. The Noachian crust is rich in basalts as well as the Hesperian and Amazonian crusts. This means that basalts have been formed probably throughout the geological history of Mars. Clearly, the methane production in the relative deep subsurface is matched by the migration of gas at shallower depths and the consequent storage of it in shallow reservoirs. This scenario does not change even in the case of biogenic production of methane because the migration and reservoir model is independent of the methane source.

Methane on Earth has two distinct and prominent reservoir stratigraphic/structural traps and gas hydrates. The former is typically the type of reservoir where the hydrocarbon production is concentrated; the latter is extensively present on Earth and the gas is entrapped in clathrates in the shallow subsurface. Both reservoirs can be present on Mars. Petroleum-style reservoirs are however not common on the planet because the geology does not have the complexity that produces this kind of reservoir. First of all, sedimentary basins with thick sedimentary successions are not present in the subsurface and also tectonics is basically weak and does not provide the formation of realms of subsidence and large horizontal translation of crust slab. Therefore, these traps are more probable on Earth than on Mars. On the contrary, gas hydrates are more likely to be formed on Mars than on Earth. The gas hydrate stability curve clearly shows that methane clathrates are stable very near the surface (Fig. 1), whereas on Earth they are stable at considerable depths. Permafrost is another element that can be useful in trapping methane on Earth. However, the terrestrial methane trapped in the permafrost is formed within the permafrost itself.

Therefore, unless there is a strong bacterial activity in the Martian permafrost, the analogy with the terrestrial permafrost is not compelling enough. However, permafrost can be a great seal for methane reservoir and methane could be present in the form of free gas or gas hydrates below a thick permafrost layer. The reservoirs would be localised in suitable areas in the crust and not homogeneously widespread all over the planet. Moreover, these reservoirs are able to remain for very long geological time scales. Methane is released them the reservoirs episodically when boundary conditions change. This scenario accounts, therefore, for an uneven distribution of methane in the atmosphere in space and time, even with an almost constant subsurface production of methane. This scenario is also robust because it is similar to the terrestrial mechanism of gas migration and storage. Biogenic gas (methane) on Earth can be produced in sediments that act also as reservoirs because this methane does not migrate. One of the best cases is the Po Plain where biogenic gas is largely exploited. This methane is young and shallow and it is contained in the source rock. Nevertheless, the transfer of this gas to the atmosphere occurs episodically and at discrete locations.

The geology of methane on Mars is as complicated as that on Earth. Nevertheless, the analogy can help in investigating the cycle of the Martian methane.

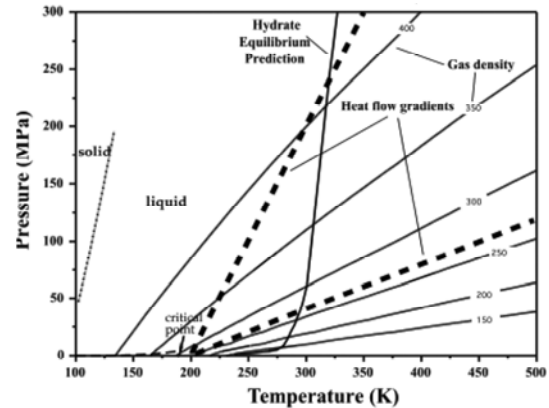**Fig. 1.** Diagram of methane phases and gas hydrate stability based on the Peng-Robinson equation of state. High (155 kWm) and low (30 kWm) heat flow gradient cases are shown. The density of the gas phase is also shown. From [3].

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METHANE EMISSIONS FROM EARTH'S DEGASSING: A REFERENCE FOR MARS.

G. Etiope, Istituto Nazionale di Geofisica e Vulcanologia, via V.Murata 605, 00143 Roma, etiope@ingv.it.

Global geo-CH$_4$ emissions and classification: Geological emissions of methane from the Earths' surface are an important global greenhouse-gas source [1], [2]. Significant amounts of CH$_4$, produced within the earth crust are released naturally into the atmosphere through faults and fractured ground. Six main geo-CH$_4$ source categories must be distinguished, in two different geological environments: 1. In petroliferous-sedimentary areas: mud volcanoes (MV), gas seeps, microseepage (invisible and diffuse exhalation from soil), submarine seepage;
2. In geothermal-volcanic areas: geothermal (non-volcanic) manifestations and volcanoes.
Major emissions are related to hydrocarbon production in sedimentary basins (microbial and thermogenic methane), through continuous exhalation and eruptions from more than 1200 onshore and shallow offshore MV (at least 6-9 Tg CH$_4$/y, globally), more than 10000 onshore seeps (3-4 Tg/y), submarine seepage (~20 Tg/y) and through diffuse soil microseepage (10-25 Tg/y) [2]. Emissions into the atmosphere related to abiogenic non-volcanic processes, such as serpentinization or mantle degassing seem to be minor; preliminary and very rough estimates suggest ~2 Tg y^{-1} [3], but they do not discriminate hydrothermal (included in the geothermal estimation) from low temperature abiogenic degassing. Global geo-CH$_4$ emission estimates range from 42 to 64 Tg y^{-1} (potentially up to 80 Tg y^{-1} [2]), which is ~10% of the total CH$_4$ emission and the second most important natural CH$_4$ source after wetlands. The global geo-CH$_4$ emissions are of the same level of or higher than other CH$_4$ sources or sinks, such as biomass burning, termites and soil uptake.

Specific fluxes: Emission factors of the several CH$_4$ source types are known thanks to hundreds of direct flux measurements [4], [5]. Macro-seep gas fluxes can cover a wide range of values. Single vents or craters of small MV (1-5 m high) can release units up to tens of tones of CH$_4$ per year. A whole MV (hosting tens or hundreds of vents) can continuously emit hundreds of tonnes per year. In all MV areas measured so far (Italy, Romania, Azerbaijan, Taiwan), the specific flux (excluding eruptions) is between 100 and 1000 tonnes km^{-2} y^{-1}. Eruptions of big MV can release thousands of tonnes of CH$_4$ in a few hours. Fluxes from individual gas seeps (natural fires, bubbling pools, independent of MV) typically range from 0.1 to 100 tonnes/year. Microseepage fluxes from dry soil are generally in the order of tens or hundreds of mg m^{-2} d^{-1} (similar to CH$_4$ fluxes in wetlands), but can reach levels of 10^3–10^5 mg m^{-2}d^{-1}, close to macro-seeps. Volcanoes are not important CH$_4$ contributors (CH$_4$ concentration in volcanic gas is extremely low) but significant fluxes can be recorded in geothermal manifestations (where CH$_4$ concentration can reach some units percent). An abiogenic, low-T serpentinization onshore seep in Turkey produces a flux exceeding 50 t/y [6].

Origin of degassing methane: CH$_4$ origin can be assessed mainly on the basis of C and H stable isotopes. A global evaluation of isotopic data from more than 140 onshore petroliferous seeps and MV indicate that about 80% of seeps release thermogenic methane and less than 4% release purely microbial gas [7]. Methane in geothermal and volcanic emission is largely inorganic, but there can be variable amounts of thermogenic gas produced by breakdown of organic matter in the rocks involved in the thermal flow. Low-T abiogenic onshore seeps are reported only in a few places [6]. Basically, at least 90% of methane emitted into the atmosphere is organic (mainly thermogenic).

Looking for analogies on Mars: Terrestrial CH$_4$ source categorization and related emission factors can be a primary reference for studies on Martian CH$_4$ sources. In particular, if MV or other gas seepage structures are identified on Mars, their size and morphological features can provide, by comparison with terrestrial analogs, first indications of the potential amount of gas released (assuming however that gas composition and pressure gradients are similar to terrestrial ones). If a global Martian CH$_4$ source of around 100-300 t/y is required to maintain a 10 ppb atmospheric level, it is clear that only a few terrestrial-type seeps may be requested. The recently discovered CH$_4$ plume in Northern Summer 2003 can be produced by an emission of at least 54 t/day [8]. On the Earth, such a source strength is provided by natural gas seepage zones of the order of 10^1-10^3 km^2 [4], such as in Azerbaijan mud volcanoes, coastal areas of the Black Sea and offshore California. But CH$_4$ could also be released by diffuse exhalation (microseepage) from Martian soil, even if macro-seeps or MV are lacking. Assuming typical microseepage from soil in petroleum basins (10-100 mg m day$_{-1}$ [4]), the plume-related 54 t/day can be provided by a microseeping area 500 to 5000 km^2 wide.

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Methane hydrates: A source for slow methane release on Mars? M.E. Elwood Madden[1], J. R. Leeman[1], B. Guttery[1], , [1]School of Geology and Geophysics, University of Oklahoma 100 E Boyd, Norman, OK, melwood@ou.edu.

Introduction: Gas hydrates (clathrates) are ice-like materials in which a guest molecule (CO_2, CH_4, ethane, butane, H_2S, etc.) is encapsulated within a rigid cage-like structure of water molecules. At elevated pressure, hydrates can form at temperatures above the freezing point of water, reaching temperatures >300K at pressures exceeding 10 MPa. On Earth, gas hydrates form in organic-rich pore waters along the continental shelf, as well as at the base of permafrost deposits associated with conventional natural gas reservoirs. Gas hydrates are also a likely phase on Mars, forming in carbon-rich regions of the subsurface [1-4]. Colder temperatures at the surface of Mars expand the latitudinal extent of hydrate-favorable regions and shift the top of the hydrate stability zone to shallower depths, relative to terrestrial environments.

Implications: Due to their composition and range of stability, hydrates have the potential to be significant subsurface reservoirs for water and carbon on Mars. The concentration of CH_4 molecules in hydrates far exceeds that in the gas phase alone- one unit volume of CH_4 hydrate contains the equivalent of 168 units of free CH_4 gas at 100 kPa and 273 K. Therefore, only 2000 m^3/yr of CH_4 hydrate would be needed to account for recent observations of CH_4 in Mars' atmosphere [5], thus small volumes of hydrates may affect atmospheric composition through formation and dissociation fluxes tied to changes in seasons, obliquity [6, 7] and/or subsurface fluid chemistry [5].

Gas hydrates may also serve as both a sink and a source of biogenic gases and/or nutrients for subsurface biological communities. Terrestrial hydrates form at the base of permafrost deposits when gas concentrations exceed the solubility limits of the hydrate phase. These environments are also likely habitability zones for subsurface microbial communities on Earth and Mars. CH_4 produced through methanogenesis may be trapped as hydrates, thus preventing biogenic gases from reaching the surface [8]. Likewise, dissociation of recent or ancient CH_4 hydrate deposits may release carbon that is then utilized by surrounding biological communities, much as CH_4 hydrate deposits support diverse ecosystems on Earth [9] .

Geologic models of hydrate reservoirs on Mars: While pressure and temperature conditions within the subsurface of Mars are conducive to gas hydrate formation, P-T conditions alone are not sufficient. CH_4 concentration must be great enough that gas hydrate is a thermodynamically stable phase, and the rate of nucleation must be sufficient for hydrates to

form within a geologic timescale. The juxtaposition of water and guest molecules of sufficient concentration within the same pore-space or fractures requires biologic or geologic processes that produce gas–saturated water or ice within a sealed, closed system [2]. Alternatively, the system could be open to the atmosphere, but in this case, a *constant* source of gas to replenish the hydrate reservoir must also exist [8].

In order to test hydrate reservoir models with observations of CH_4 flux and surface features on Mars, the kinetics of hydrate formation and dissociation processes at Mars-relevant conditions must be determined. Data available for ice-hydrate transformations is very limited and often contradictory since terrestrial hydrate forms predominantly through liquid-gas interactions. The Gas Hydrates Laboratory at the University of Oklahoma is currently conducting low temperature, moderate pressure experiments to determine the rate of hydrate formation and dissociation below the freezing point of water.

Terrestrial analog experiments have demonstrated that hydrate formation and dissociation are both self-limiting processes. The endothermic nature of hydrate dissociation requires additional heat flow to sustain hydrate dissociation. In addition, the large volume change coupled with gas release from hydrate dissociation results in elevated pressures within closed or semi-closed systems, effectively halting further hydrate dissociation. Therefore, natural hydrate melting rates are likely to be slow, especially at low temperatures.
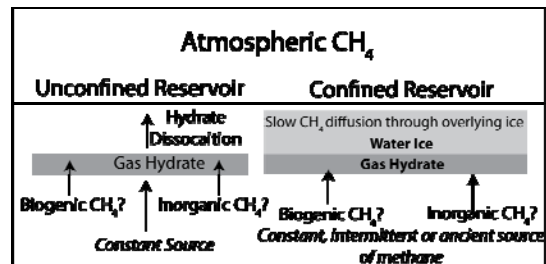
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METASTABLE METHANE CLATHRATE PARTICLES AS A SOURCE OF METHANE TO THE MARTIAN ATMOSPHERE.

E. Chassefière, Université Versailles St-Quentin; UPMC Univ. Paris 06 ; CNRS/INSU, LATMOS-IPSL, Université Pierre et Marie Curie, Boite 102, 4 Place Jussieu, 75005, Paris, France, e-mail : eric.chassefiere@latmos.ipsl.fr

Introduction: The recent detection of methane at an average ≈20-30 ppb level in the Martian atmosphere from Mars Express and Earth-based observations [1,2] suggests that methane currently is being produced. Methane may have different origins: volcanism, hydrogeochemical/thermal activity, biological activity, external supply by meteorites and comets. From several lines of evidence, Mars is still internally active, with a potential for continuing magmatic-driven activity, including volcanism and hydrothermal activity. One possibility is that methane is produced through low temperature alteration by a hydrothermal alteration of basaltic crust [3]. Independently, it has been suggested that methane might originate in subsurface clathrate layers [4]. Such clathrate layers are expected on Mars, and large amounts of methane can be stored for long periods of time in these layers. In the present paper, we suggest that methane is released from subsurface clathrate layers, but under the form of metastable clathrate particles, which further decompose and release free gaseous methane to the atmosphere. Hydrothermal activity could be at the origin of methane involved in clathrate layer formation [4]. Hydrothermal production of methane [3] could therefore be the original source of methane, stored in a first step in the subsurface, then released to the atmosphere under clathrate form and decomposed to gaseous methane.

Methane release process: The observations of methane made by the PFS instrument onboard Mars Express [5,2] exhibit a correlation between methane mixing ratio and water vapor mixing ratio (Fig. 1).

left), latitude (upper right) and longitude (lower right) [7].

The recent data obtained from ground-based telescopes [2] 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 it 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 [6]. 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 [7]. 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 (Fig. 2). 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. This value of 6 months is in good agreement with the recent estimate made by using a General Circulation Model [8] to reproduce local methane enhancements observed from Earth [2]. The reason why methane has a short lifetime might be the occurrence of heterogeneous chemical decomposition of methane in the subsurface [7], where it is known since Viking biology experiments that oxidants efficiently decompose organic matter.
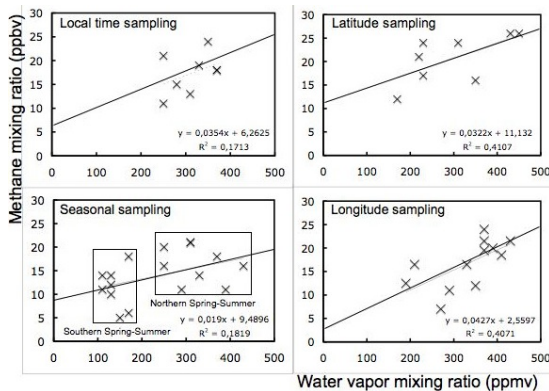

Fig. 1 : Methane mixing ratio as a function of water vapor mixing ratio , and correlation straight lines and parameters, for four sets of Mars Express PFS data [5] providing the variations of methane and water vapor mixing ratios as a function of local time (upper left), solar longitude (lower
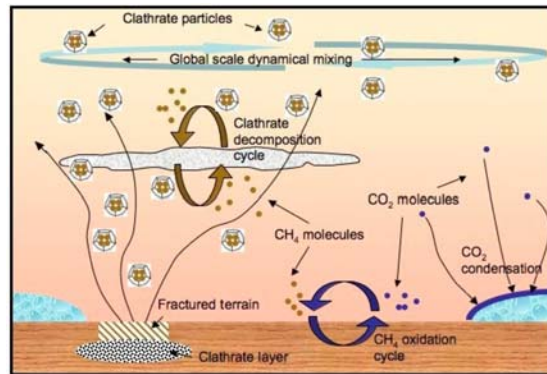

Fig.2: Schematic diagram of the carbon cycle (Clathrate-CH_4-CO_2) on Mars according to the proposed explanation [7].

The present source of methane clathrate, acting over the last few hundred thousand or million years, could have given rise to the thin CO_2-ice layer covering the permanent water ice south polar cap.

Possible implication of the short methane lifetime for the depth of the subsurface oxidation layer: It is known that, in terrestrial soils, H_2O_2 is decomposed through a number of aqueous reactions [9]. One of them, of particular interest for the Martian case, is the Fe-catalyzed Haber-Weiss reaction :

$$O_2^- + H_2O_2 \rightarrow O_2 + OH + OH^-$$
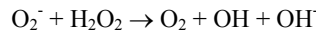
which is catalyzed by ferric iron, for example occupying a site at an oxide surface. In the absence of any molecule able to reduce OH, OH reacts with H_2O_2 according to the reaction :

$$OH + H_2O_2 \rightarrow H_2O + O_2^- + H^+$$
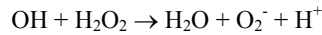
and the net reaction is :

$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$$
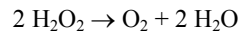
This mechanism produces OH in the course of H_2O_2 decomposition, and the precise yield of OH depends on the relative amounts of redox-active species. In terrestrial soils, it has been shown that organic and inorganic constituents may react with OH in place of the H_2O_2, thus decreasing the rate of H_2O_2 decomposition. Due to the high content of ferric oxides in Martian subsurface, it may be thought that H_2O_2 is similarly decomposed, with some OH radicals being formed at the surface of pores, and rapidly released to the subsurface atmosphere. Experiments performed on terrestrial soils [9] show that the OH formation efficiency through H_2O_2 decomposition varies substantially among soils, being in the range from 1% to 30% depending on the iron and organic matter content of samples. One of the main questions for Mars, still to be solved by laboratory work, is to know which proportion of hydrogen peroxide present in the subsurface is under the form of free OH radicals, produced by Fe-catalyzed Haber-Weiss reaction. Assuming, for matter of illustration, that this proportion is 1%, the concentration of OH in the subsurface is 10^9-10^{10} larger than in the global atmosphere, yielding a lifetime of CH_4 in the subsurface of a few seconds.

According to existing models [10], the amount of H_2O_2 in the close subsurface, mainly under adsorbed form, is $\approx$100-200 nmol/cm^3 in the few first centimeters or meters below the surface, which represents a very large amount. We suggest that H_2O_2 in the subsurface is decomposed by atmospheric methane, which prevents hydrogen peroxide from penetrating below a superficial layer of $\approx$1 cm depth [7]. If so, H_2O_2 would be inefficient in oxidizing the subsurface. Methane would therefore act as an inhibitor of the oxidation of subsurface material by hydrogen peroxide. This result, if confirmed by laboratory work, would have strong implications for future Mars exploration. A thin superficial oxidation layer makes theoretically possible to find unaltered organic matter at centimetric depth in the Martian soil.

What to do now?: It is first necessary to check and precise through laboratory work the hypothesis proposed in this paper, that is the stability of small clathrate particles in Martian atmospheric condition. Second, the processes of the decomposition of clathrates in the Martian atmosphere, in presence of water vapor close to supersaturation, must be characterized, in terms amplitude and kinetics. In parallel, accurate modeling using General Circulation Models, and a simple parametrization of the clathrate decomposition, can allow to determine the best parameters in view of preparing the interpretation of future data. From this point of view, only an orbiter of Mars equipped with a powerful set of spectrometers (infrared, microwave), will allow to significantly progress in our understanding of Martian methane processes. A precise modeling, supported by a detailed map of methane (including vertical profiles), could possibly allow to localize source regions of clathrates at the surface if they are sufficiently localized and intense. Precise measurements of the oxidation state (adsorbed hydrogen peroxide, oxidized minerals) of the superficial regolith, with a sub-centimetric vertical sampling capability, from future landers could provide crucial information on the mechanisms of methane oxidation in the subsurface.

The measurement of the carbon isotopic ratio ($\delta^{13}C$), as already proposed for CH_4 [3], in both methane and carbon dioxide of the atmosphere would be of high interest. If most of the atmospheric CO_2 comes from the oxidation of CH_4, the $\delta^{13}C$ of CO_2 could reflect the $\delta^{13}C$ of CH_4. The in-situ analysis of cores sampled in the permanent south polar cap, providing the record, as a function of depth, of the isotopic ratio of carbon in the superficial carbonic ice layer, could also provide information on the chronology of methane outgassing.

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THE TRAPPING OF METHANE IN MARTIAN CLATHRATES HYDRATES. C. Thomas, O. Mousis, S. Picaud and V. Ballenegger, Institut UTINAM, CNRS-UMR 6213, Université de Franche-Comté, Besancon, France (caroline.thomas@univ-fcomte.fr)

Introduction: Recent observations have evidenced traces of methane (CH_4) heterogeneously distributed in the Martian atmosphere [1], [2], [3], [4]. However, because the lifetime of CH_4 in the atmosphere of Mars is estimated to be around 300-600 years on the basis of photochemical reactions [1] [3], its actual sources remain controversial. Among other assumptions, it has been proposed [5] that clathrate hydrates located in the subsurface of Mars could be at the origin of the small quantities of CH4 detected.

Thermodynamic approach: To calculate the relative abundance of CH_4 incorporated in clathrates formed from the martian atmosphere, we use the same approach as in our previous studies devoted to the trapping of gases by clathrates on Titan [6], [7]. This approach is based on the statistical model proposed by van der Waals and Platteuw [8]: in this formalism, the relative abundance f_G of a guest species G in a clathrate (of structure I or II) is defined as the ratio of the average number of guest molecules of species G in the clathrate over the average total number of enclathrated molecules, as :

$$f_G = \frac{b_L y_{G,L} + b_S y_{G,S}}{b_L \sum_J y_{J,L} + b_S \sum_J y_{J,S}},$$

where the sums in the denominator run over all species present in the system, and b_S and b_L are the number of small and large cages per unit cell, respectively. The occupancy fractions y_G of the guest species G for a given type of cage and for a given type of clathrate are determined from the Langmuir constants which are related to the strength of the interaction between each guest species and each type of cage. Thus, this statistical approach relies on the accurate determination of the interactions between the guest species G and the water molecules forming the surrounding cage. In a first approximation, this cage is assumed to be spherical and the corresponding interactions are represented by a spherically averaged Kihara potential, the integration of which within the cage giving the Langmuir constants.

This statistical approach has been used to study the composition of clathrate hydrates formed in the near subsurface of Mars as a function of temperature, from a plausible composition of the gas.

Six different initial abundances of methane in the gas phase have been considered in the present study (0.01%, 0.1%, 1%, 10%, 50% and 90%). The largest values are typical of methane-rich conditions in which CH_4 is supplied from below by microbial or geological processes or from above from ancient atmospheres. In contrast, the lowest values are more typical of recent atmospheric compositions.

Results: Our results [9] show that in presence of CO_2, a methane-rich clathrate hydrate can be thermodynamically stable only if the gas phase is itself strongly enriched in methane. Hence, CH_4-rich clathrate hydrates cannot be formed from the present martian atmosphere, which has been found to be very poor in methane. As a consequence, if they do exist, CH_4-rich clathrate hydrates on Mars should have been formed in contact with an early martian atmosphere, much richer in CH_4 than the present one.

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VARIABILITY OF ATMOSPHERIC METHANE INDUCED BY ADSORPTION IN THE REGOLITH.

P.-Y. Meslin[1], R. Gough[2], F. Lefèvre[3], F. Forget[1], M.A. Tolbert[2], [1]Laboratoire de Météorologie Dynamique, Univ. Paris 6, BP 99, 75005 Paris, France (pymlmd@lmd.jussieu.fr),[2]Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309. [3]LATMOS, CNRS/UPMC, Paris, France.

Introduction: The observed variability of methane concentrations in the atmosphere of Mars [1] raises severe challenges regarding its origin. It implies both a strong spatial and temporal variability of the source of CH_4 and some very efficient destruction processes that do not have their terrestrial counterparts [2]. Recent numerical simulations with the LMDZ Global Circulation Model (GCM) have shown that known atmospheric chemical and physical processes are unable to produce the observed distribution of methane [3]. The observed variations imply the existence of a loss process that is 600 times faster than predicted by standard photochemistry. An atmospheric lifetime of less than 200 days (assumed uniform with height) is indeed required, compared to a lifetime of 330 terrestrial years obtained with a standard photochemical model. If the yet unknown loss mechanism of CH_4 is a surface process, an even shorter lifetime is required (a few hours only) [3].

Variability due to adsorption in the regolith: Another source of variability that will necessarily affect the atmospheric fields of CH_4 on a seasonal timescale is the adsorption of this gas in the regolith, as suggested by [4]. The cold wintertime surface temperatures increase the adsorption coefficient in the topmost meters of the subsurface and a net transport of CH_4 from the atmosphere to the regolith is expected to occur until a new adsorption equilibrium is reached (or at least approached). This excess of CH_4 (compared to the equilibrium value corresponding to the mean surface temperature) is subsequently released to the atmosphere during summertime. As adsorption is fully reversible, this regolith "breathing" induces both spatial and time variability without the need for additional sources and sinks, thus avoiding difficulties raised by other scenarios. In addition to the expected latitudinal variations (controlled by the insolation), variability will also be induced by differences in soil thermal inertia and specific surface area, which control the amount of gas stored in the seasonal subsurface reservoir. Experiments performed on a Martian soil analog have shown that the adsorption of CH_4 to mineral surfaces could both kinetically and thermodynamically account for the reported seasonal and spatial variability in CH_4 concentration [4,5]. The approach followed in [5], however, does not formally take into account atmospheric transport and vertical mixing. Therefore, it is necessary to have recourse to a coupled subsurface-atmosphere GCM to better characterize the effect of adsorption on the atmospheric CH_4 fields and to confirm its efficiency (both in terms of kinetics and amount of gas exchanged).

Model description: A subsurface transport model has already been implemented in the LMDZ GCM to study the subsurface-atmosphere exchange of water vapor and radon [6,7]. It solves the adsorption-diffusion equation with appropriate boundary conditions and treats the adsorbed and gas phases as two distinct tracers. These two phases are coupled through transfer coefficients whose temperature dependence needs to be specified and is taken from [5]. This allows us to take into account both the kinetics of adsorption and the kinetics of diffusion. In practice, if the characteristic time for adsorption is much smaller than the one for diffusion, the two phases are always in adsorptive equilibrium (as given by the adsorption isotherm). A linear adsorption isotherm is assumed, which is well-suited for trace gases such as methane. For instance, the surface coverage for CH_4 under Martian conditions is less than 1.5×10^{-7} [5]. By default, first-order loss terms are included for the two phases but are set to zero for methane. Oxidative solid-gas reactions could therefore be included in the future, but are believed to be extremely limited for CH_4 under Martian conditions [1].

Scenarios investigated: Two scenarios will be investigated. Firstly, the effect of temperature-induced seasonal variations will be characterized by assuming a uniform subsurface flux of CH_4 consistent with a steady-state atmospheric concentration of ~10 ppbv and a photochemical lifetime of 330 years. In such a scenario, the adsorbed phase varies seasonally but is on average in equilibrium with the atmospheric concentration. Secondly, the fate of an episodic, localized release of methane, occurring on top of the above scenario (supposed to represent a standard state), will be analyzed. In particular, the time needed to adsorb the excess amount of atmospheric CH_4 and to reach a new adsorption equilibrium will be determined. The effect of the specific surface area will also be investigated. Comparison to observations should provide new constraints on the exchange of volatiles with the subsurface.

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CHALLENGES RAISED BY THE OBSERVED VARIATIONS OF METHANE ON MARS. F. Lefèvre[1]
and F. Forget[2], [1]LATMOS, UPMC Univ. Paris 06, CNRS, F-75005 Paris, franck.lefevre@upmc.fr, [2]LMD,
UPMC Univ. Paris 06, CNRS, F-75005 Paris, francois.forget@lmd.jussieu.fr.

Introduction: The detection of methane on Mars [1-3] 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 appears to be locally enhanced and changes 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. We used a global climate model of Mars with coupled chemistry to examine the implications of the recently observed variations of Martian methane for our understanding of the chemistry of methane [5].

Method: Methane chemistry was implemented in the Laboratoire de Météorologie Dynamique (LMD) global climate model (GCM) of Mars with on-line photochemistry [6]. In the 'conventional' atmospheric chemistry scheme, which explains correctly the observed distribution of methane on Earth, loss of methane on Mars occurs primarily by photolysis at heights above 60 km, and by oxidation by OH and $O(^1D)$ at lower altitudes. These constituents are produced respectively by the photolysis of water and ozone. The LMD GCM was integrated at a resolution of 3.75° latitude × 5.625° longitude, on 32 vertical levels from the ground up to about 120 km.

Results: we first initialized the GCM with a uniform mixing ratio and monitored the exponential decay of methane in a long-term simulation that did not include any source. We find that the global atmospheric mass of methane is reduced by a factor of *e* after 330 terrestrial years. From this estimation, the source flux of methane at the Martian surface must be 260 tonnes per year for a steady-state value of 10 ppbv. To investigate the possibility that such a source can create variations in the observed methane field, we introduced a highly localized and sporadic release in the GCM. We chose the area and timing of this release to coincide with the important local maximum observed [3] in northern summer 2003: methane is released at the surface in a single grid cell of the model located in Syrtis Major and the emission is assumed to occur for only 60 sols around solar longitude $L_s = 150°$. We find that the local release of methane does not produce any significant enhancement or plume in the source region. In contrast with the observation, the model shows an essentially well-mixed distribution over the most of the planet. A striking feature, however, is the large methane enrichment that results from the condensation of CO_2 gas at high southern latitudes, which

appears to be in good quantitative agreement with the argon enhancement measured by GRS [7].

To create variations other than those due to CO_2 condensation, a considerably more intense source is required. This in turn implies a greater sink, and hence a shorter lifetime in order to maintain the same quantity of methane in the atmosphere. To determine this lifetime, we released idealized tracers from the region of Syrtis Major where enhanced methane was observed in 2003. We find an optimal agreement with the observations if the release is episodic (60-120 days) and if the gas has an atmospheric lifetime of about 200 terrestrial days. Such a lifetime implies that the methane loss in the atmosphere is about 600 times faster than predicted by the standard chemistry. The existence of such a fast loss in the Martian atmosphere is difficult to reconcile with the observed distribution of other trace gas species. Additionally, the amount of methane released during the sporadic event must be of the order of 150 000 tonnes, which is comparable to the yearly geochemical production of methane by serpentinization (50,000–130,000 tonne yr^{-1}) along the entire Mid-Atlantic Ridge on Earth [8]. 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 a few hours to explain the observations. If the 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.

This talk will give an overview of these results. Using dedicated GCM simulations, we will also discuss the mechanisms that have been recently proposed to explain the reduced lifetime and unexpected variability of methane on Mars.

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A SHORT-LIVED TRACE GAS IN THE MARTIAN ATMOSPHERE: A GENERAL CIRCULATION MODEL OF THE LIKELIHOOD OF METHANE.

Malynda R. Chizek[1], James R. Murphy[1], Melinda A. Kahre[2], and Robert M. Haberle[2], Giuseppe A. Marzo[2], [1]New Mexico State University, Las Cruces, NM 88003, USA, (mchizek@nmsu.edu), [2]NASA Ames Research Center, Moffett Field, CA 94087, USA.

Introduction: Recent detections of trace gas concentrations in Mars' atmosphere at wavelengths consistent with methane (CH_4) [1,2,3,4] raise intriguing questions about the source(s) of that gas, and the desire to more strictly constrain the specific gas(es) being detected. We are using numerical atmospheric modeling to investigate surface source magnitudes (and spatial and seasonal extents) consistent with the observed gas concentrations, destruction times that can reproduce the seasonality of the observed gas abundances, and other thermodynamic characteristics of the Mars atmosphere/surface system that might aid in identifying the gas(es) being detected.

Background: CH_4 (or a gas with a similar spectral signature) was first detected in the Martian atmosphere in 2004 [2,3] from both ground based and spacecraft observation. Formisano et al. (2004) and Krasnopolsky et al. (2004) estimated an atmospheric column mixing ratio of ~10 parts per billion (ppb). Formisano et al. determined mixing ratios varying between 0 and 30 ppb over the planet, with an average of 10 ppb during the period of observations (January to May 2004).

Mumma et al. (2009) have more recently detected spectral features consistent with CH_4 via ground based observations and conclude that the magnitude of CH_4 abundance changes on a seasonal timescale (observations at L_s 17˚, 121˚, and 155˚) and is spatially variable. Their maximum mixing ratio values (~45 ppb at L_s 155˚) exceeded the values estimated by [2] and [3].

Fonti and Marzo (2009) have recently investigated three Martian years of MGS TES spectra to reveal a temporally and spatially variable spectral feature at 1306 cm^{-1} (7.6 μm), coincident with CH_4 bands. Their results span a wider seasonal range than those of [1], and are globally extensive, and also suggest a northern summer maximum in gas abundance.

GCM Simulations: Lefevre and Forget (2009) have investigated the photochemical destruction time of a trace gas using a highly localized and sporadic CH_4 source within simulations conducted with the Laboratorie de Meteorologie Dynamique global climate model (GCM). They use episodic releases lasting 60 sols, and show that the spatial and temporal variability in the observations cannot be reproduced without an atmospheric lifetime shorter than 200 days.

Our work: We are using the NASA Ames GCM (Version 1.7.3) to constrain the magnitude, spatial extent, and duration of a surface trace gas source, and the destruction (by photochemical or other loss mechanisms) rate of that gas, required to reproduce the observations of [1] and [4].

Mumma et al. proposed that a surface CH_4 source magnitude of 0.6 kg s^{-1} and a source ~10^{13} km^2 in extent centered in Syrtis Major could, under conditions of diffusive mixing, 'fill' their observed plume in an appropriate time interval. Simulation results with those source specifications produced column gas mixing ratio values more than one order of magnitude less than detected by [1]. This result arises because the simulated advection of the introduced gas is much more efficient (gas is more rapidly dispersed away from the source region) than the diffusion coefficient suggested in [1]. A source magnitude ~30 times more intense is required to produce column abundance values that agree with those of [1]. This same source magnitude also produces column mixing ratio patterns globally which are in reasonable agreement with those of [4], except for their preferred Tharsis source region. The above results arise with a destruction time of ~0.5 Earth years, which is consistent with the results of [5].

The seasonal time of source activation can be constrained by [1] and [4] to initiate after L_s 17˚ but prior to early northern summer, and to persist at least through middle northern summer. Additional simulations will be conducted to investigate when the source activity must begin and end in order to agree with all observations. We will investigate other gases (including nitric acid) which have similar spectral features but potentially other loss mechanisms (such as condensation).

From the model, we determine the parameters which constrain the behavior of the gas. These constraints can show whether the observed gas can realistically be CH_4, which would require destruction processes much more robust than photochemical lifetimes, or whether it must be another gas with different removal processes.

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ARGON: THE MIXING STANDARD FOR METHANE IN MARS ATMOSPHERE. A. L. Sprague[1] and W. V. Boynton[1], [1]Lunar and Planetary Laboratory, The University of Arizona, 1629 E. University Blvd. Tucson, AZ 85721 (sprague@lpl.arizona.edu, wboynton@lpl.arizona.edu).

Introduction: Methane (CH_4) is a gas that will not condense in the atmosphere or on the surface at Mars' temperatures. It therefore belongs as a member in a larger group of noncondensable gasses: argon (Ar), nitrogen (N_2), oxygen (O_2), and carbon dioxide (CO). Argon, N_2 and CO are observed to vary temporally and spatially despite the absence of short timescale sources and sinks [1, 2, 3]. For example, although the total Ar in the atmosphere is constant, the observed concentration of Ar varies by many factors (up to 10) on short (dozens of sols) and seasonal timescales [1]. This is because the amount of carbon dioxide (CO_2) in the atmosphere changes by as much as 30% over a Mars year because of seasonal condensation and sublimation from the polar caps and high latitude regions. Ar and other non-condensables are enhanced in concentration as a result of temporary confinement within the polar vortices, and are diminished in concentration because of rapid dilution from subliming CO_2 frost and transport controlled by topography.

In addition, retrievals of CO mixing ratios from measurements by The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard the Mars Reconnaissance Orbiter (MRO) spacecraft show the seasonally and globally averaged CO mixing ratio to be 700 ppm, but with strong seasonal variations at high latitudes. The summertime near-polar CO mixing ratio falls to 200 ppm in the south and 400 ppm in the north because of dilution by CO_2 as it sublimes from the seasonal polar ice caps. At low latitudes, the CO mixing ratio varies in response to the mean seasonal cycle of surface pressure [3]. This behavior is similar to that of equatorial Ar, the mixing ratio of which is measured from the APXS on MER-B in dedicated atmospheric measurements [4].

CH_4 distributions and abundance: Methane detection [5, 6, 7] and subsequent detailed mapping of its abundance and distribution in Mars' atmosphere show it to be positively correlated with water vapor [8] and sometimes concentrated over discrete locations on the surface [9]. A suggestion of an atmospheric source of CH_4 from metastable submicronic particles of methane clathrate hydrate continuously released to the atmosphere has been proposed to explain details related to the observations [10]. For example, based on the CH_4 abundances found in ground-based observations at different times of year, and the use of an atmospheric eddy mixing model, it is found that the mean CH_4 mixing ratio would be higher (~ 6ppb) than that actually observed (~ 3ppb). Thus, it is suggested [9] that the actual lifetime of CH_4 in the atmosphere is less than the photochemical lifetime computed from standard atmospheric chemical models [6].

Global Circulation Model (GCM) experiments [11] have followed the distribution and abundance of a localized release of CH_4 in an amount similar to that observed [9] and find methane to be quickly well mixed but then enriched along with other non-condensables during polar night. No similar distribution between CH_4 and H_2O vapor abundance as that observed [8] is found. Other regional enrichments are also predicted but unrelated to the localized source.

Argon, the standard against which to measure differences: The variability in CH_4 may be influenced by as yet unknown sources and poorly understood photochemistry in Mars' atmosphere. But it remains unknown how much of its variability is simply a result of atmospheric transport. Observed spatial and temporal Ar variations in Mars' atmosphere [1] have proven to be an unexpected and valuable tracer for atmospheric circulation, especially at high southern latitudes. In the absence of strong sources and unusually rapid photochemical destruction, CH_4 should exhibit spatial and temporal variability similar to that exhibited by Ar, N_2, O_2, and CO [1, 2, 12, 3]. By binning the Ar data in short timescale and in special latitude and longitude increments, we can provide a detailed study of noncondensable fluctuations within overall circulation patterns. Such variability may give insights with respect to the observed CH_4 concentrations and may reveal important new details regarding the movement and deposition of dust, water vapor, other inert gases, especially CH_4.

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The spatial and temporal variation of oxidant component in the Martian atmosphere observed by MEX/PFS.

S. Aoki[1], Y. Kasaba[1], I. Murata[1], H. Nakagawa[1], V. Formisano[2], M. Giuranna[2] and A. Geminale[2]. [1]Department of Geophysics, Tohoku University, Sendai, Miyagi 980-8578, Japan. [2]I. F. S. I. , INAF, Via Fasso del Cavaliere 100, 00133 Rome, Italy.

Recently, a small amount of CH_4 was discovered in the Martian atmosphere [1][2][3]. Although various theories about its source, i.e., biological, volcanic, etc., have been proposed, it is still an open question. In a recent study, the seasonal variation of CH_4 was found [4]. Because the variation time scale is shorter than that expected from the photochemical dissociation of CH_4, the oxidation loss due to strong oxidants (OH etc.) in the low altitude becomes strong candidate to cause the variation. H_2O_2 is one of the indices for strong oxidants. There is a theory of the 200 times enhancement of the H_2O_2 production by the atmospheric electric discharge with turboelectric process of dust grains associated with dust storm or dust devil [5]. The season of CH_4 decrease almost corresponds to that of dust storm [4][6]. Such indirect ideas suggest the importance of the survey of H_2O_2 in the Martian atmosphere.

The observations of H_2O_2 in the Martian atmosphere are only three cases, and the observed abundance is 0-50 ppb [7][8][9]. In order to search more detailed time and spatial variations, we try to derive the seasonal and spatial variations of H_2O_2 in the data taken by Planetary Fourier Spectrometer (PFS) aboard Mars Express (MEX).

The data calibration has been achieved by the cooperation with the PFS PI team. In past ground-based observations, the observed spectral range for H_2O_2 was 1200-1300 cm^{-1}. However, on the PFS spectral resolution, the CO_2 absorption too much contaminates the H_2O_2 absorption in this range. We have selected the 300-400 cm^{-1} spectral interval, in which there are a lot of strong H_2O_2 lines and few CO_2 . Although the absorption of H_2O is still major component, the 100ppb of H_2O_2 can be detected with SNR of 10 by averaged of 2000 measurements at the 362 cm^{-1}. The method of the retrieval is (1) to retrieve the thermal radiation from surface and dusts, (2) to retrieve the H_2O column abundance at the wavenumbers with strong absorption of H_2O, and (3) with the fixed thermal spectrum and H_2O absorption features, to retrieve the H_2O_2 column abundance at the wavenumbers with strong absorption of H_2O_2.

By the method, we have been retrieving the seasonal variation of two areas. One ranges from -50° to +50° latitude, the other ranges from +-50° to +-90° latitude. The former, low and middle latitude area is where the abundance of H_2O_2 is relatively low [9] but thermal radiation from the Martian surface is relatively strong. The latter, high latitude area is where the abundance of H_2O_2 is relatively high [9] but thermal radiation from the Martian surface is relatively weak. We will show the first result of seasonal variation of H_2O_2, and compare the seasonal variation of H_2O_2 with that of CH_4 using same data set together with the PFS PI-team.

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UNUSUAL CO BEHAVIOUR IN MARTIAN ATMOSPHERE. A RELATION TO METHANE?

V.Formisano , A. Geminale and G.Sindone , IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it and Giuseppe.sindone at ifsi-roma.inaf.it).

Abstract: CO is produced in Martian atmosphere by photodissociation of CO2. This process should produce large quantities of CO, which are not observed. Water vapour photochemistry produces the mechanism that brings CO back to CO_2. Therefore CO and H_2O are anticorrelated in Martian atmosphere. This is particularly true in northern summer, when, the sublimating northern polar cap brings large quantities of water into the atmosphere.

On average in summer, PFS-MEX has observed this anticorrelation which is evident also in the work of Smith et al 2009.[1] In summer, however, they report unusual large quantities of CO in the northern hemisphere, at certain longitudes, up to the polar regions. CO enrichment in polar regions is usually related to the CO2 condensation, which, however, occurs in winter, while these observations are in summer.

Also PFS has observed this anomalous behaviour of CO: in a number of orbits, going toward the northern polar regions, the mixing ratio of CO increases TOGHETHER with the water vapour mixing ratio, H_2O reaching up to 1600 ppm, and CO reaching even more than 1000 ppm. This fact can only be understood in terms of a source of CO, probably clathrate hydrate in the water ice of the polar cap.

These observations raise two questions : were is this CO coming from, and is it related to methanogenic production of methane?

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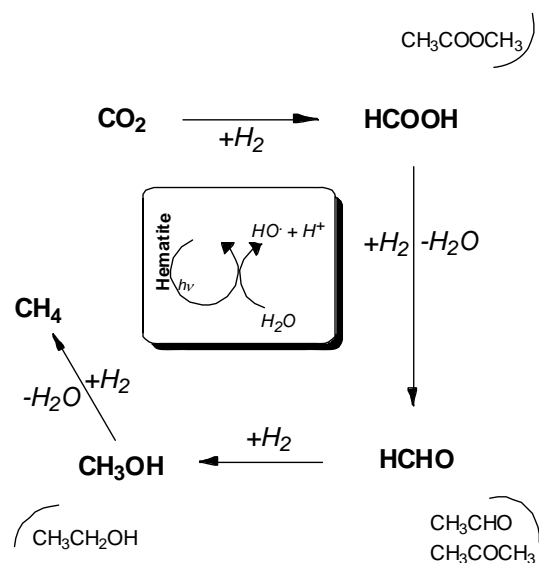
PHOTOCHEMICALLY INDUCED FORMATION OF MARS-RELEVANT OXYGENATES AND METHANE FROM CARBON DIOXIDE AND WATER.

M. Bartoszek[1], M. Wecks[2], G. Jakobs[1] and D. Möhlmann[3], [1]Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, D-18059 Rostock, Germany, e-mail: michael.bartoszek@catalysis.de, [2]Institut für Nichtklassische Chemie e.V., Permoserstr. 15, D-04318 Leipzig, Germany, e-mail: wecks@inc.uni-leipzig.de, [3]Institut für Planetenforschung, Deutsches Zentrum für Luft- und Raumfahrt, Rutherfordstraße 2, D-12489 Berlin, Germany, e-mail: dirk.moehlmann@dlr.de

Introduction: The concentration of formaldehyde in the atmosphere of Mars was found to be tenfold higher than that of methane. This contradicts to the short lifetime of formaldehyde if compared to methane. Additionally, a connection between appearance of methane, formaldehyde and water in distinct regions of Mars was found. Inspired by the discussion about possible sources of methane and formaldehyde in the atmosphere of Mars, the transformation of carbon dioxide to oxygenates involving UV irradiation under laboratory conditions was investigated.

The aim was to investigate relationships of available carbon dioxide and (at least temporarily present) liquid interfacial water on the one hand and the influence of semiconductor materials like hematite as relevant planetary surface material on the other, with respect to the possible formation of oxygenate molecules under UV irradiation. It is assumed that hematite can act as a photocatalyst both under laboratory conditions and also at the surface of Mars.

Formation of Oxygenates: The irradiation of carbon dioxide with UV-light in the presence of water results in the formation of C, O, and H containing molecules which could be detected by GC-MS.

The experiments were carried out under atmospheric pressure and room temperature. Oxygenates with one carbon atom like formaldehyde and methanol were found, but also C_2- and C_3-species like acetone.

The role of hematite seems to be ambivalent. Hematite has a significant influence on the distribution of the products. Additionally, the conversion of carbon dioxide increases in the presence of hematite. Note, however, that most of the oxygenate species also appear without hematite in the reaction cell.

Experiments with ^{18}O-labelled water show a transfer of oxygen from water to carbon which results in labelled oxygenate molecules.

As shown in the Scheme 1, oxygenates could be formed from CO_2 via photocatalytic reduction processes. The observed formation of C_2- and C_3-species might point to secondary competitive and consecutive reactions via complex and less selective mechanisms.

All these results give hints to different reaction mechanisms, and support the assumption that both photocatalytic and radical reactions contribute to the formation of oxygenates from carbon dioxide and water by UV-irradiation. More importantly, the results give indication of a potential formation of hydrocarbons such as methane via conversion of carbon dioxide and water on Martian mineral interfaces. Nevertheless, it is certainly necessary to gain more and quantitative insight into the contribution of photocatalytic processes to the apparent presence of oxygenates and hydrocarbons in the near surface atmosphere of Mars.

Scheme 1: Possible reaction pathways from carbon dioxide to oxygenates and methane via photocatalysis on hematite.

THE PHOTOCHEMISTRY AND ATMOSPHERIC LIFETIME OF METHANE ON MARS FOR EVOLVING ATMOSPHERIC CONCENTRATIONS OF CARBON DIOXIDE AND THE VARIABILITY OF THE MARS PLANETARY BOUNDARY LAYER (PBL) BASED ON MEASUREMENTS FROM THE VIKING 1 AND 2 LANDERS, MARS PATHFINDER AND PHOENIX.

J. S. Levine[1], M. E. Summers[2], J. A. C. Burdette[3] and D. S. Holz[4]
[1]Science Directorate, NASA Langley Research Center, Hampton, VA 23681, joel.s.levine@nasa.gov
[2]Dept. of Physics and Astronomy, George Mason University, Fairfax, VA 22030, msummers@gmu.edu
[3]Dept. of Physics, East Tennessee State University, Johnson City, TN 37614
[4]Dept. of Physics, Wilkes Honors College, Florida Atlantic University, Jupiter, FL 33458

Introduction: The presentation will cover three areas related to methane on Mars: (1) The structure of the Mars planetary boundary layer (PBL), (2) The photochemistry of methane on Mars, past and present, and (3) A new platform for the measurement of atmospheric methane, a robotic, rocket-powered airplane.

Measurements: We present an investigation into the structure and variability of the Mars planetary boundary layer based on temperature, pressure, wind speed and wind direction measurements obtained by the Viking 1 and 2 Landers, Mars Pathfinder and Phoenix. The Mars PBL is important in the methane transport process whether methane is produced biologically or geologically it will transported from the surface and/or subsurface into the atmosphere through the PBL.

Calculations: Using a one-dimensional photochemical model of the atmosphere of Mars, we have investigated the atmospheric chemistry and lifetime of methane and other trace atmospheric gases for a wide range of atmospheric carbon dioxide concentrations ranging from the present atmospheric concentration to 100 x the present atmospheric concentration. There is considerable speculation that in its early history, the mass of the atmosphere of Mars was considerably greater than the present-day atmosphere. Subsequently, Mars lost a significant amount of its original atmosphere via the "sand-blasting" effect of the solar wind, once Mars lost its planetary dipole magnetic field, which originally protected the atmosphere from the solar wind interaction.

Future Measurements of Methane: Proposed measurements of atmospheric methane from a robotic, rocket-powered airplane will be discussed. The airplane flying about a mile above the surface can cover many hundreds of miles of horizontal distance. A mass spectrometer in the airplane can obtain measurements of atmospheric methane concentration, the methane concentration gradient and the isotopic composition of the methane.

MARS ATMOSPHERIC CIRCULATION AND CHEMISTRY DETECTED IN THE SUBMM DOMAIN.

P. Hartogh[1], [1]Max-Planck-Institut für Sonnensystemforschung, Max-Planck-Str. 2, 37191 Katlenburg-Lindau, Germany, hartogh@mps.mpg.de

Abstract: This presentation will provide an overview about recent findings of the Mars atmospheric modeling group at MPS (e.g. [1], [2], [3] and [4]) and how a number of unsolved science questions will be addressed by submm sounding of the Martian atmosphere from space.

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SEARCH FOR IMPORTANT MINOR GASES IN MARTIAN ATMOSPHERE

A. Geminale and V.Formisano . IFSI-INAF, Roma, Tor Vergata, Italy (vittorio.formisano at ifsi-roma.inaf.it and anna.geminale at ifsi-roma.inaf.it).

Abstract:

In this paper we search for some important minor gases that could clarify the origin of methane in Martian atmosphere. These minor gases are C_2H_6, methanol, acetic acid.

Abiotic origin of methane in Martian atmosphere refers to the so called "serpentinization" mechanism. This mechanism, which is supposed to occur underground in presence of relatively high temperatures, requires silicate rocks (i.e. olivine) in presence of acquifer (H_2O liquid). The resulting chemical reaction should generate not only methane (CH_4) but also $1/n(C_nH_m)$ [1]. The observation of 20 ppbv of methane , should go together with 10 ppbv of C_2H_6.

This gas has a band at 2976 cm-1, with an important Q-branch that should be measurable by PFS-MEX, specially if many spectra are averaged to increase the SNR.

We compare synthetic spectra computed for 10,20,50,100 ppbv of C_2H_6 with 3 big averages of 89000, 27000 and 5200 PFS spectra with increasing amount of methane. No indication of C_2H_6 is present in the spectra, therefore an upper limit of only 10 ppbv can be put in the 3 cases having 15 , 25, and 35 ppbv of methane.

The search for methanol is essentially not possible because a strong methanol feature is always present in the spectra due to contamination of the pointing mirror. Methanol was used in the lab on ground to clean some parts of the hardware.

We shall refer also about other minor gases of interest.

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SEARCH FOR HYDROGEN PEROXIDE IN THE MARTIAN ATMOSPHERE.

.V.Formisano, A.Geminale, IFSI-INAF, Rome, Italy
Y.Kasaba, S.Aoki,Tohoku University, Japan

Abstract: The lifetime of methane in Martian atmosphere against photochemical destruction has been evaluated to be 300-600 years (Wong et al 2003)[1]. For this reason methane is expected to be uniform and constant in time for different seasons. Methane has been observed to change substantially with space and season, therefore a strong sink must be considered, and consequently a stronger source (see Lefebvre and Forget 2009)[2]. Vast quantities of H_2O_2 could be produced during dust storms and could be hidden in the first few cm of the soil (Atreya et al 2007)[3]. Atreya computed that up to 4 ppm of H_2O_2 could be produced during storms because of electrostatic charging of dust grains. If so much hydrogen peroxide exists in the few cm of the soil, is it possible that some of it will escape to the atmosphere, changing the mixing ratio of 10-30 ppbv predicted by the photochemistry?

We considered 5 spectra obtained as averages over many orbits, in order to increase the SNR, and we have searched in the [300, 450] cm^{-1} wavenumber range, covered by PFS-MEX, for H_2O_2 lines not covered by water vapour lines. The 5 average spectra were at different Ls.

Four spectral lines of the H_2O_2 have been found suitable for this study as do not overlap with water vapour: at 362, 380, 416 and 433 cm-1. The first one of these seems to be the most reliable. The average mixing ratio is 117 ppbv varying from 70 ppbv to 180 ppbv, with a standard deviation of 37 ppbv. Strong variations were found also in the same spectrum from one line to the other, and the reason is not understood (possibly the quality of the fit or the instrumental response function) . If only the first line is considered, than a small variation with season can be seen, with 90 ppbv of H_2O_2 in northern spring and 150 ppbv in southern summer (when dust storms are more frequent).

Our conclusion is that the H_2O_2 is a few times higher than the photochemical value. This can be explained if we assume that a minor fraction of the peroxide generated around dust grains can be released from the soil to the atmosphere.

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Search of SO2 in the Martian atmosphere by ground-based submillimeter observation.   Hiromu Naka-gawa[1], Yasumasa Kasaba[1], Hiroyuki Maezawa[2], Akira Hashimoto[1][3], Hideo Sagawa[4], Isao Murata[1], Shoichi Okano[5], Shohei Aoki[1], Nayuta Moribe[2], Akira Mizuno[2], Munetake Momose[6], Toshikazu Ohnishi[7], Norikazu Mizuno[8], Tomoo Nagahama[2]

[1] Department of Geophysics, Tohoku University, Sendai, Miyagi 980-8578, Japan.

[2] Solar-Terrestrial Environment Laboratory, Nagoya University, Nagoya, Aichi 464-8601, Japan.

[3] NEC TOSHIBA Space Systems, Japan.

[4] Max Planck Institute for Solar System Research, 37191 Katlenburg-Lindau, Germany.

[5] Planetary Plasma and Atmospheric Research Center, Tohoku University, Sendai, Miyagi 980-8578, Japan.

[6] Institute of Astrophysics and Planetary Sciences, Ibaraki University, Bunkyo 2-1-1, Mito, Ibaraki 310-8512, Japan

[7] Physical Science, Graduated School of Science, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

[8] ALMA Project Office, National Astronomical Observatory of Japan, National Institutes of Natural Sciences, 2-21-1 Osawa, Mitaka, Tokyo 181-8588, Japan

Introduction: With increased knowledge on our neighbor planets Mars and Venus based on re-cent aggressive explorations, their images are chang-ing significantly. In particular, Mars, called as 'a frozen water planet', is almost certain that Mars once had a duration with warm and wet climate. It still conserves a large amount of water ice under the sur-face. The question "Why and when did they di-verge?" is essential for their environments which could potentially create and keep the life or not.

It is clear that volcanism had occurred through-out much of history of Mars [1][2]. The release of gases into the atmosphere due to volcanism may have had significant climatic effects. The result is seen in the abundance and widespread distribution of sulfates on the surface as detected by recent lander missions [3]. While the effect of atmospheric sulfur dioxide (SO_2), which is one of several greenhouse gases for the terrestrial case, on early Martian cli-mate is still quite speculative, it seems clear that SO_2 could have played a significant role in episodic warming of Mars [4].

The current Martian volcanic and crustal activi-ties are still under debatable. A firm understanding for their activities is essentially dispensable to clarify both of the gas production, which shall be connected to the origin of the Martian CH_4. In this study, we focus on a sensitive search for Martian sulfur oxide (SO and SO_2) with the higher-dispersion spectro-scopic observation in submillimeter range.

Observation and Result: We searched sulfur oxide (SO_2 and SO) in the Martian atmosphere by the Atacama Submillimeter Telescope Experiment (ASTE). Sulfur oxide is one of the most evident spe-cies in terrestrial volcanic gases. Although it has not yet detected at Mars, this detection can constraint the Martian crustal and volcanic activities. We observed northern winter of Mars on 26 December 2007 ($Ls = 8.1°$) in 346 GHz range with ~ 1 hour integration. We get the upper limit of the SO_2 mixing ratio, 2 ppb. This is mostly equivalent to the value observed in northern summer ($Ls = 205°$) [5]. We concluded that the crustal or volcanic gas produced into the atmosphere is tenuous in northern winter. Obtained upper limit can also restrict the CH_4 production by recent volcanic activities. The sub-observer longi-tude (210º to 299ºW) of our observation covered the regions where CH_4 appears notable localized in northern summer [6]. It is significant that the evi-dence for SO_2 could not be found in the atmosphere in the area of CH_4 accretion. Because it is unlikely to consider the volcanic gases without SO_2 in Mars, our result restricts the production of volcanic gases from the Martian surface into the atmosphere, and is against the source of CH_4 from volcanic and crustal gas. Some kind of non-volcanic carbon hydride source shall possibly be under the Martian surface.

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THE FORMALDEHYDE OBSERVATIONS OF 1969 AND 1989: ANALYSIS OF THE OBSERVATIONS AND PROPOSALS FOR INTERPRETATION.

C.Muller and D. Moreau, Belgian Institute for Space Aeronomy (IASB-BIRA) and B.USOC, avenue circulaire, 3, B-1180 Brussels, Christian.Muller@busoc.be, Didier.Moreau@busoc.be

Introduction: In 1969, the first detailed infrared spectrum of Mars was obtained by Reihard Beer of the Jet Propulsion Laboratory using the Mount Palomar telescope and showed some features which at the time were described as similar to formaldehyde. When the PHOBOS mission to Mars was designed, the Soviet channel of the AUGUSTE optical package included an infrared limb sounder in the same wavelength whose purpose was to measure the vertical distribution of HDO in the Martian atmosphere. Two PHOBOS spacecrafts were launched but only one could operate during a few Martian orbits and showed formaldehyde absorptions corresponding to a layer centered at 17 km of altitude, this communication will address the value of these observations, the possible artifacts that could have been in the data and will present some explanations in the methane current controversy and why methane could not have been observed at the occasion of these observations.

History: Formaldehyde plays an important role in prebiotic chemistry. It was accidently discovered by Butlerov in 1859 and this chemist discovered also the formose reaction by which sugars found later to be present in RNA are produced. Its production processes do not limit themselves to the oxidation of methanol in the presence of a catalyst, they are varied and different for all cases, ranging from purely inorganic synthesis to direct biological production. Formaldehyde was first discovered in earth in tropical rain waters by Dhar and Ram (1932), the observation was repeated later at several locations on earth but the frequent remote validated measurement of formaldehyde came only in beginning in 1995 when the GOME instrument on ERS-2 and the SCIAMACHY instrument on ENVISAT began a systematic mapping using the DOAS (differential optical absorption spectroscopy) technique. The sources of terrestrial formaldehyde are essentially biomass burning and the oxidation of methane. The first discovery of formaldehyde in the solar system was made in 1986 when the VEGA spacecraft encountered the Halley comet and that the IKS Franco-Russian instrument observed formaldehyde in the comet. However, formaldehyde production had been considered for a very long time in the Venus atmosphere by mechanisms involving carbon dioxide and hydrogen sulfide, it is now still to be observed.

Martian observations: The 1969 Mount Palomar spectrum of Reinhard Beer covered the 3 micrometer range because it is an atmospheric window on the earth, the earth atmosphere was eliminated through divsion by a moon spectrum and the mars spectra showed a reproducible set of features corresponding to what was known of the formaldehyde spectrum at the time, however the corresponding publication stated that the feature observed could not be attributed to formaldehyde due to the high value necessary. Later in 1976, VIKING substantiated these arguments by showing that not only no organics were present in the surface soil but even that it contained a powerful unknown oxidant incompatible with any complex molecule.

The PHOBOS mission was a very sophisticated two spacecraft mission and one the objectives of its Franco-Russian optical package was to analyze the escape of water and thus was able to differentiate heavy water from ordinary water in several intervals. Some elements of the design were similar to the national Belgian instrument of the defunct ESA Kepler satellite and it is in this context that it was decided at the highest level in IKI to add this instrument to the Belgian-Soviet space cooperation programme which had been initiated in 1987. Unfortunately, only one of the spacecrafts arrived at the planet and obtained a limited set of observations. This short communication will describe these operations in term of formaldehyde observations and the various explanations that have been proposed since methane oxidation is not a sufficient source to account for the retrieved values. The instrument did not observe methane but no measurement were obtained below 5 km of tangent height. The layering of formaldehyde points to an atmospheric production process possibly involving heterogeneous chemistry.
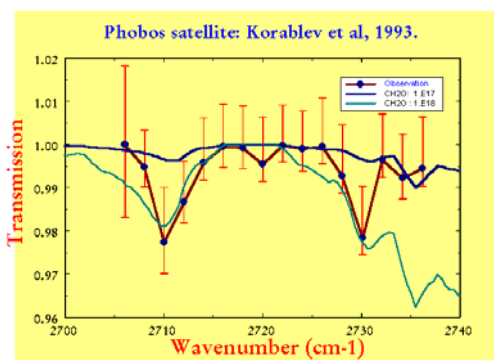

Fig.1: formaldehyde spectrum from Korablev et al (1993), the altitude distribution of the feature defers from CO2, ruling out an isotopologue of CO2.

Microbial Life in Ice: Habitats, Metabolism, and Survival on Mars

P. Buford Price, Univ. of California at Berkeley

Microbes, including methanogens, may have originated in glacial ice [1]. If so, they could live in liquid veins at grain boundaries [2], on clay grains in ice or permafrost [3], or even within an ice crystal lattice [4]. Microbes in terrestrial ice have been shown to metabolize at a rate proportional to exp(-Q/RT) that is just sufficient to repair spontaneous macromolecular damage [5,6]. Their lifetimes are constrained mainly by the dose rate from alpha particles from Th and U impurities in soil and rock [7]. Putative Martian microbes, if encased in low-radioactivity ice, may have survived to the present day. In order for methanogenic metabolism to account for the time-varying methane flux on Mars, they probably live less than a few hundred meters below unconsolidated soil today. If the methane bursts are mainly of microbial origin, their present concentration can be estimated as a function of temperature and burial depth. Other gaseous products of microbial metabolism such as N_2O should be sought in spatial and temporal coincidence with methane bursts [6].

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Methenogenesis on Earth today: where, who and how D. Prieur, Laboratoire de Microbiologie des Environnements Extrêmes. University of Brest. IUEM. 29270 Plouzané, France. Daniel.prieur@univ-brest.fr

Methanogenesis on Earth is the result of abiotic anb biotic processes. In the latter cases, prokaryotic micro-organisms belonging to the Archaea Domain are exlusively responsible for methane production. Methane is the final product of enzyme-mediated reactions, carried out by Methanogens for energy production. Energetic substrates are di-hydrogen, but also various acetate or methyl containing compounds. Methanogens thrive in various anaerobic habitats (sediments, muds, rocks, hot springs, digestive tracts, etc) and , according to the species, live in cold, mild or very hot environments.

The aim of this paper is to summarize available knowledges on biotic production of Methane on Earth, in order to produce guidelines and references for detection of biotic production of Methane on Mars. Taxonomic diversity, phylogeny, physiology, enzymology and activities of methanogens on Earth will be reviewed.

The possibility of methane oxidation coupled to microbial perchlorate respiration

John. D. Coates
Department of Plant and Microbial Biology, UC Berkeley

Oxidation of methane by microorganisms on Earth is known to occur under both aerobic and anaerobic conditions with nitrate, ferric iron, and sulfate as alternative terminal electron acceptors. Under aerobic conditions, the activity of methanotrophic microorganisms is absolutely dependent on the presence of atmospheric molecular oxygen. This is because these organisms not only utilize O_2 as their sole electron acceptor for energy production, but also require molecular oxygen as a co-substrate for the central metabolic enzyme, methane monooxygenase (MMO), which transforms methane into methanol as the first step in the pathway. In contrast, known anaerobic metabolism of methane is mediated by complex syntrophic interactions between unknown "reverse methanogenic Archaea" and various hydrogenotrophic autotrophic respiratory organisms capable of utilizing nitrate, Fe(III), or sulfate as terminal electron acceptors.

Alternatively, the unusual metabolic capabilities of microorganisms utilizing perchlorate as a terminal electron acceptor may also be capable of directly oxidizing methane without the need for atmospheric oxygen or a syntrophic partner organism. This is because this unique metabolism, although anaerobic, produces molecular oxygen as a transient intermediate, which is potentially bioavailable for other cell processes involving oxygen-dependent enzymes such as the methane monooxygenase. Our previous studies have shown that molecular oxygen produced by dissimilatory perchlorate reducing bacteria (DPRB) is bioavailable for the microbial metabolism of recalcitrant hydrocarbons such as naphthalene and benzene when incubated in co-culture with obligate aerobic hydrocarbon oxidizing organisms. More recently we have isolated a perchlorate reducing bacterium, *Dechloromonas aromatica* that is capable of directly oxidizing monoaromatic hydrocarbons coupled to perchlorate reduction in the absence of a partner organism. Whole genome sequencing of *D. aromatica* revealed the absence of any genes known to be involved in anaerobic hydrocarbon metabolism but the presence of an entire oxygenase-dependent aerobic pathway suggesting that this organism mediates hydrocarbon oxidation using O_2 biogenically produced from perchlorate reduction.

Although no known DPRB isolated to date have been shown to be capable of methane oxidation, the studies described above suggest that such a metabolism is highly likely. DPRB have been isolated from a broad diversity of environments including both pristine and contaminated soils and sediments. Although originally unexpected due to the supposed limited natural abundance of perchlorate, recent geochemical studies have indicated that natural perchlorate is far more prevalent than originally perceived. Considered to primarily be of anthropogenic origin because of its extensive application in industrial processes, its widespread discovery in pristine environments and recently in Martian soils at concentrations as high as 1-3% by mass has indicated a more complex natural biogeochemical origin. This has raised several important questions regarding a biogeochemical redox cycle of chlorine on Earth and the possibility for life on Mars. Although the exact mechanisms of natural perchlorate neogenesis are unknown, it is thought that they are based on oxidative atmospheric chemistry involving UV radiation and Cl_2 gas. In contrast, perchlorate diagenesis primarily occurs through microbial metabolism. Phenotypic characterization revealed that the known DPRB exhibit a broad range of metabolic capabilities including the oxidation of hydrogen, simple organic acids and alcohols, hexoses, reduced humic substances, and electrically charged cathodes. Of potentially more importance to Martian environments, several of these organisms have also been shown to use simple hydrocarbons, both soluble and insoluble ferrous iron, hydrogen sulfide, and elemental sulfur.

DPRB are ubiquitous on Earth, dependent on molybdenum for their metabolism, and the presence of atmospheric oxygen or soluble nitrate negatively regulate perchlorate reduction. All DPRB are members of the proteobacteria, a phylum that is believed to have evolved 2.5 – 2.8 Ga. However, molecular evidence suggests that perchlorate reduction is the result of horizontal gene transfer events and it may not have originated in the proteobacteria phylum. This is supported by evolutionary analysis of the genes specifically involved in the metabolism, the perchlorate reductase and the cytochrome oxidase, both of which are belonged to protein families that may have been prevalent in the last universal common ancestor 4.25 – 4. 29 Ga suggesting that perchlorate reduction may have evolved earlier than the recognized host organisms in the proteobacteria.

The field of microbial perchlorate reduction has significantly advanced in a very short period from a poorly understood metabolism to a burgeoning scientific field of discovery. Over the last 10 yrs we have gained a much greater appreciation of the microbiology, biochemistry and genetic systems involved, however, very little is known of this metabolism in more extreme environments on Earth or terrestrial analogs of Martian soils where it could potentially play a role in the biological oxidation of methane.

A sub-zero Arctic methane seep: implications for Mars methane. T. D. Niederberger[1], N. N. Perreault[1,2], S. Tille,[3] B. Sherwood Lollar[3], G. Lacrampe-Couloume,[3] D. T. Andersen[4], C. W. Greer,[2] W. Pollard[5], L. G. Whyte[1*].
[1]Natural Resource Sciences, McGill University, St. Anne de Bellevue, QC, Canada, H9X 3V9.
[2]Biotechnological Research Institute, National Research Council of Canada, Montreal, QC, Canada, H4P 2R2.
[3]Stable Isotope Laboratory, University of Toronto, Ontario, Canada, M5S 3B1. [4]SETI Institute, California, USA, 94043. [5]Department of Geography, McGill University, QC, Montreal, Canada, H3A 2T5.
*Corresponing and Presenting Author (Lyle.Whyte@McGill.ca)

Introduction: It has been recently postulated by Mumma et al., [1] that the 10 ppb methane reported in the Mars atmosphere [2] may originate from localized "hotspots" or "plumes" of methane arising from the Martian surface. The origin of these plumes is under debate and could be attributable to either geological or biological sources, the latter including methanogenesis by microbial communities inhabiting the Martian subsurface. Here we report the first geophysical and microbiological characterization of the only known terrestrial methane seep in a cryo-environment on Earth in the form of a hypersaline (~24% salinity), sub-zero (-5ºC), perennial spring, arising through thick extensive permafrost in an area with an average annual air temperature of -15°C and with air temperatures below -40°C common during the winter months. This site not only provides a model of how a methane seep can form in a cryo-environment but also a mechanism for the hypothesized Martian methane plumes. Our results also provide evidence that this hypersaline, subzero environment supports a viable microbial community capable of activity at temperatures as low as -10ºC, and that the methane itself may act as an energy and carbon source for sustaining anaerobic oxidation of methane-based microbial metabolism, rather than methanogenesis, within these extreme environmental constraints.

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METHANOGENS: A MODEL FOR LIFE ON MARS. T A. Kral[1,2], T.S. Altheide[2], A.E. Lueders[1], T.H. Goodhart[1], B.T. Virden[1], W. Birch[1], K.L. Howe[2] and P. Gavin[2], [1]Dept. of Biological Sciences, University of Arkansas, Fayetteville, AR, [2]Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR.

Introduction: The relatively recent discoveries that liquid water most likely existed on the surface of Mars (1) and that methane currently exists in the Martian atmosphere (2, 3, 4) have fueled the possibility of extant or extinct life on Mars. One possible explanation for the methane in the Martian atmosphere would be the presence of methanogens in the subsurface. Methanogens are microorganisms in the domain Archaea that can metabolize molecular hydrogen as an energy source, carbon dioxide as a carbon source, and produce methane.

For the past 16 years, we have been studying methanogens as a model for life on Mars (5, 6, 7, 8, 9). In 1998 (5), we demonstrated that methanogens could exist on relatively low concentrations (down to 15 ppm) of molecular hydrogen, their primary energy source. Theoretically, molecular hydrogen is present, but if not, carbon monoxide has been measured in the Martian atmosphere, and some methanogens can use this in place of molecular hydrogen as an energy source. In 2004 (6), we presented evidence that certain methanogens could grow on a Mars soil simulant (JSC Mars-1). This has been important in trying to simulate the Martian subsurface.

Here we present evidence that certain methanogenic strains can metabolize or survive under a number of conditions present on Mars. These include metabolism at low pressure on JSC Mars-1, metabolism in the presence of perchlorate salts, metabolism using carbonate as a carbon source, and survival following desiccation at Earth-surface pressure (1 bar) as well as Mars-surface pressure (6 mbar).

Methods: The methanogens tested were *Methanothermobacter wolfeii, Methanosarcina barkeri, Methanobacterium formicicum* and *Methanococcus maripaludis*. The low-pressure metabolism experiments were performed in the Andromeda Chamber while the low-pressure desiccation experiments were performed in the Pegasus Chamber. Both vacuum chambers are located at the Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville. In the low-pressure metabolism experiments, cells were in water-saturated JSC Mars-1. Pressures utilized were 400 mbar and 50 mbar. In the low-pressure desiccation experiments, dried cells were distributed on glass beads (control) or on Martian analog substrates (JSC Mars-1, basalt, montmorillonite, nontronite, jarosite) in open culture tubes. For the perchlorate and carbonate experiments, cultures were grown in standard methanogenic growth media containing the test compounds in anaerobic tubes. The 1 bar desiccation experiments were carried out in desiccators in a Coy Anaerobic Chamber. The dried cells were sitting in open microcentrifuge tubes (1.5 ml) at room temperature in an atmosphere of CO_2 (88%) and H_2 (12%). In all cases, methane was measured by gas chromatography.

Results and Discussion: With respect to metabolism at low pressure on JSC Mars-1, significant methane production was observed for *M. wolfeii, M. barkeri* and *M. formicicum* at both 400 mbar and 50 mbar for up to two weeks (the limiting factor was the availability of liquid water). Even though there are reports of organisms surviving at low pressures, this is one of the first reports of organisms actively metabolizing at these pressures. *M. maripaludis* was not tested in this experiment.

In 2008, The Phoenix Lander detected both perchlorate (10) and carbonate (11) at its landing site. In the presence of perchlorate salts (sodium, magnesium and potassium), all four species of methanogens produced substantial levels of methane, even in the presence of 1% (wt/vol) perchlorate salt. When $CaCO_3$ (1% [wt/vol]) was the sole source of carbon, *M. wolfeii, M. barkeri* and *M. formicicum* were all able to produce methane, although at much reduced levels compared to cells supplied with CO_2.

In the 1 bar desiccation experiments, *M. barkeri* survived up to 330 days (so far). *M. formicicum* survived 180 days while *M. wolfeii* survived 120 days. In the 6 mbar desiccation experiments, *M. wolfeii, M. barkeri* and *M. formicicum* survived 120 days (the longest period tested) while *M. maripaludis* survived only 60 days, all on glass. With respect to survival on Martian analog substrates in the desiccated state, *M. barkeri* was the only methanogen tested that survived on multiple substrates.

Overall, the results reported here would seem to indicate that methanogens, as we know them, may be able to survive and possibly thrive in the Martian subsurface.

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METHANOGENIC ACTIVITY IN RIO TINTO, A TERRESTRIAL ANALOGUE OF MARS.

R. Amils[1,2], N. Rodriguez[1], J.L. Sanz[2], [1]Centro de Astrobiología (CSIC-INTA), carrt Ajalvir k4, 28850 Torrejón de Ardoz, Madrid, Spain, ramils@cbm.uam.es, nrodriguez@cbm.uam.es and [2]Centro de Biología Molecular Severo Ochoa (UAM-CSIC), U. Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain, jose-luis.sanz@uam.es.

Abstract: Río Tinto (SW, Spain) holds unusual characteristics of low pH (mean value 2.3), oxidant redox potential (+440mV) and high concentration of heavy metals [1,2]. Due to its geochemistry dominated by iron and sulfur minerals, e.g. jarosite, hemathite and goethite, is considered an interesting geochemical Mars analogue [3,4]. As corresponds to its extreme conditions, the prokaryotic diversity, which is now well characterized, is rather low [5]. Methanogenic archaea are generally found in habitats with reductive (negative) redox potentials and pH close to neutrality, which in principle exclude them from the Tinto ecosystem. Methane generation was observed in different sites along the river [6] and also in the drilling wells of the MARTE project [7]. Methane generation was observed in microcosms operating with sediments from the Tinto basin. Methanol, formate, volatile fatty acids and lactate added to these microcosmos stimulated the production of methane. In all cases the methane released was associated with a decrease in the redox potential to negative values and with an increase in pH. Cores from a sampling site with deep sediment accumulation from Río Tinto were taken. These cores showed characteristic well-defined black bands in the midst of otherwise brown-red sediments. *Methanosaeta concilii* was detected directly in the black bands. In enrichment cultures, *M. concilii* (medium supplemented with complex substrate), *Methanobacterium bryantii* (supplemented with H2) and *Methanosarcia barkeri* (supplemented with methanol) were identified. These results indicate that the ability of methanogens to thrive in the Tinto basin is due to the generation of mildly acidic reducing micro-niches in the river´s sediment. Iron reduction catalyzed by bacteria like *Acdithiobacillus ferrooxidans* and *Acidiphilium* spp., both present in the Tinto ecosystem, or even methanogens themselves [8], can be involved in this phenomenon. These results demonstrate that in the mineralogical and chemical conditions detected on Mars underground methanogenic activity can be performed opening the possibility that the short life methane recently observed on Mars [9] is of biological origin, which obviously will have to be proven in future exploration missions.
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BACTERIAL SURVIVAL IN MARTIAN CONDITIONS. G. Galletta[1,2], G. Bertoloni[3], M. D'Alessandro[4] and R. Visentin[3], [1]Department of Astronomy, University of Padua, e-mail: giuseppe.galletta@unipd.it, [2] CISAS "G. Colombo", University of Padua, [3]Department of Histology, Microbiology and Medical Biotechnologies, University of Padua, [4]INAF - Osservatorio Astronomico di Padova.

Terrestrial lifeforms show a strong capability to adapt to very harsh environments and to survive even to strong shocks as those derived from meteorite impacts. These findings increase the possibility to find traces of life on a planet like Mars, that had past conditions similar to the early Earth but now is similar to a very cold desert, irradiated by intense solar UV light.

Finding Martian environment conditions that allow the survival of lifeforms may have a double meaning: increasing the hope to find extraterrestrial life and defining the limits for a terrestrial contamination of planet Mars.

To test this survival, we designed and built two simulators of Martian environments where to perform survival experiments of terrestrial bacteria strains: LISA (Laboratorio Italiano Simulazione Ambienti) [1], that allows six simultaneous experiments, and a single-experiment version of it (mini-LISA). Our LISA environmental chambers can reproduce the conditions of many Martian locations near the surface [2,3].

Inside LISA we have studied the survival of several bacterial strains and endospores. We found that some *Bacillus* strains have a particular capability to survive in Martian conditions without screening by dust or other shields (see next Figure).
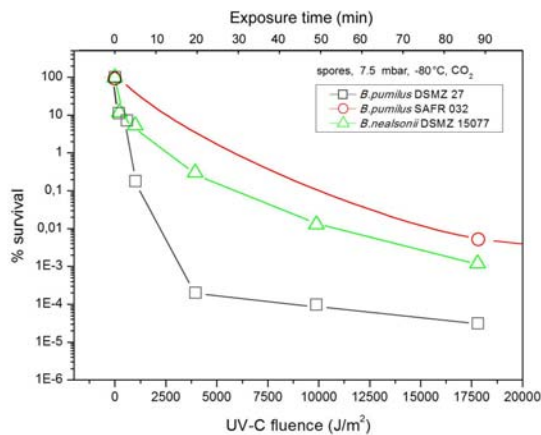
We verified that the UV light is the major responsible of cell death, Neither the low temperature or pressure, nor the desiccation or the atmospheric changes were effective in this sense. Cell not exposed to UV have a higher survival rate (see next Figure)
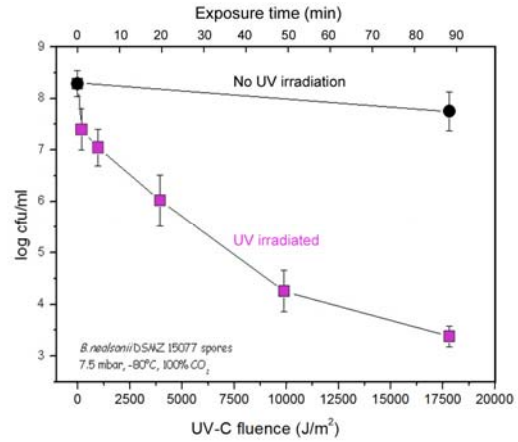
We also simulated the dust coverage happening on the real planet by blowing on the samples a very small quantity of volcanic ash grains or red iron oxide dust. Samples covered by these dust grains have shown a high percentage of survival, indicating that under the surface dust, if life was present on Mars in the past, some bacteria colony could still be present.

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ZERO-VALENT IRON ON MARS: AN ALTERNATE ENEREGY SOURCE FOR METHANOGENS.

Brendon K. Chastain[1], Timothy A. Kral[1], [1]University of Arkansas, Dept. of Biological Sciences, SCEN 601, Fayetteville, AR 72702, bkchasta@uark.edu.

Introduction: The most common form of methanogenic metabolism involves the utilization of H_2 for energy and CO_2 for carbon [1, 2]. Like all organisms, methanogens also require various trace metals and micronutrients to survive. Previous work in our laboratory has shown that the trace metals and micronutrients available in montmorillonite clay can support methanogenic metabolism when appropriate carbon and energy sources are supplied [3]. It is known that Mars offers abundant CO_2, but the status of H_2 availability is uncertain [4, 5]. However, zero-valent iron (Fe^0) has been confirmed on the surface of Mars and may also exist in the subsurface [6, 7, 8]. It is known that cathodic depolarization in Fe^0 can shuttle electrons to protons in solution and supply molecular hydrogen for methanogenic metabolism [9]. With this in mind, an experiment was designed to determine whether methanogens could survive in anaerobic microenvironments containing CO_2, montmorillonite, and Fe^0.

Methods: The following methanogenic species was used: *Methanothermobacter wolfeii*. Acid-washed glassware was used throughout the study. Cells were centrifuged and washed twice with sterile buffer to help minimize residual nutrient carryover. The cells were then suspended in sterile bicarbonate buffer and injected into sterile, anaerobic tubes containing only montmorillonite or montmorillonite and Fe^0. The bicarbonate buffer served as a carbon sourced for the organisms. Four replicate microenvironments containing Fe^0 and four controls containing no Fe^0 were monitored for methane production. Gas chromatography was used to analyze headspace composition.
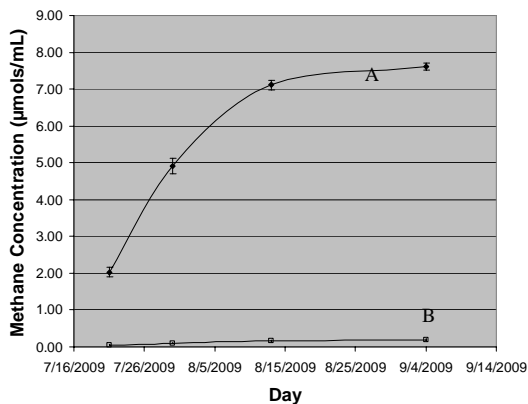
Results: *M. wolfeii* showed dramatic methane production in the presence of Fe^0, but virtually no methane production in controls (Figure 1). By the fourth week of the study, the headspace above microenvironments containing montmorillonite, Fe^0, and bicarbonate buffer contained an average of 7.11 +/- 0.13 µmol/mL (MEAN +/- S.E.M. [n=4]) methane. In comparison, microenvironments containing only montmorillonite and bicarbonate buffer showed average headspace methane of only 0.15 +/- 0.03 µmol/mL. Some slight, short-term methane production was expected in controls due to H_2 carryover from the anaerobic preparation chamber. Future work will likely involve pulling a soft vacuum on tubes after initial preparation and re-pressurization with pure CO_2.

Discussion: These results show that methanogens can use a mixture of elemental iron and montmorillonite to support methanogenic metabolism in conditions somewhat similar to those present on Mars. This work confirms the ability of methanogens to survive on Fe^0/H^+-derived hydrogen when their other nutritional requirements are supplied by CO_2 and montmorillonite, a Mars-relevant smectite. However, this study focused solely on the $Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$ reaction and neglected the possibility that a $4Fe^{2+} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2$ reaction might also sustain methanogenic metabolism. If such a phenomenon occurs in H_2-deficient environments, it could have important implications for Mars, a planet where ferrous minerals are abundant [10, 11]. Indeed, rust-colored deposits, indicating possible oxidation of Fe^0 to the ferric state, were present in our microenvironments after only a week (Fig. 2). Identification of these deposits will take place at the conclusion of this study. Investigations utilizing methanogens and ferrous minerals in Mars-like environments are also planned.

Figure 1. Methane production by *M. wolfeii* in microenvironments containing Fe^0 (A) versus those lacking Fe^0 (B).

Figure 2. Microenvironments showing possible indications of Fe^0 oxidized to the Fe^{3+} state. All tubes are identical with the exception of 1 gram of Fe^0 added to the four tubes on the left.

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GROWTH AND BIOMEDIATED MINERAL ALTERATIONS BY METHANOGENS UNDER GEOCHEMICAL CONDITIONS SIMILAR TO THE MARTIAN SUBSURFACE.

Brendon K. Chastain[1], Timothy A. Kral[1], Vincent F. Chevrier[2], and Travis S. Altheide[2], [1]University of Arkansas, Dept. of Biological Sciences, SCEN 601, Fayetteville, AR 72702, [2]Arkansas Center for Space and Planetary Sciences, bkchasta@uark.edu.

Introduction: As we go forward with astrobiological missions to Mars, the identification of advantageous landing and research sites is of extreme importance. "Following the resources" is an obvious mantra in the search for appropriate sites. Mars has plentiful carbon in the form of CO_2, and the possibility of subsurface H_2 gas has been established [1, 2, 3]. Based on the following, methanogens have been suggested as a terrestrial analog of organisms that might be found in the martian subsurface:

1) Methanogens have the ability to utilize CO_2 and H_2 as their sole carbon and energy sources [4],

2) Small amounts of methane have been detected in the martian atmosphere [5, 6, 7],

3) Some methanogens have the ability to fix nitrogen, thereby addressing the potential "nitrogen dilemma" on Mars [8].

The points listed above are important, but an organism's **micronutrient requirements** should not be neglected in discussions of targeted research locations. Availability of micronutrients is vital to an organism's survival. With this in mind, we initiated investigations of methanogens' ability to extract necessary micronutrients from materials similar or identical to those existing on Mars. The results have stimulated investigations into possible alternative metabolic pathways that might occur in Mars-like environments.

Methods:
Three species of methanogens were used:
Methanobacterium formicicum
Methanosarcina barkeri
Methanothermobacter wolfeii

Methanogenic cells were centrifuged and washed three times with sterile bicarbonate buffer to help minimize residual nutrient carryover. The cells were then suspended in sterile buffer and injected into sterile, anaerobic tubes containing Mars regolith analog. Bicarbonate buffer and hydrogen gas provided carbon and energy. The tubes were periodically pressurized with CO_2 and H_2. Gas chromatography was used to analyze headspace composition. Organisms were transferred to new substrate tubes when substantial methane was detected. This helped exhaust residual nutrients possibly stored during growth in the initial stock culture. Two transfers of these cultures were performed.

The following Mars regolith analogs were tested and compared to a sterile buffer control over a period of eight months:
Jarosite
Nontronite
Montmorillonite
JSC Mars-1 [9]
JSC Mars-2 [10]

Results: Graphical representations of data collected during the eight-month study are shown below (Figs. 1, 2, 3). The two marked peaks on each graph indicate when culture transfers occurred. Drops in methane concentration subsequent to the second transfer are due to periodic re-pressurization with H_2 and/or CO_2. Statistical analysis of final means showed methane production rates significantly greater than the control in the following substrate tubes:

M. formicium: Montmorillonite
M. barkeri: Montmorillonite, JSC Mars-1
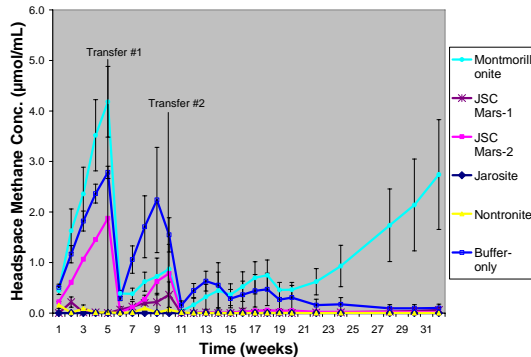*M. wolfeii*: Montmorillonite, JSC Mars-1

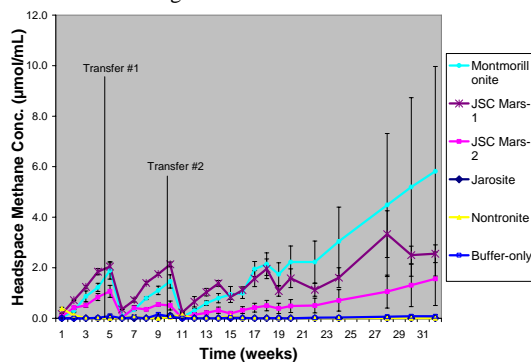Figure 1: Methane production by *M. formicicum* on various Mars-relevant geochemical substrates.

Figure 2: Methane production by *M. barkeri* on various Mars-relevant geochemical substrates.
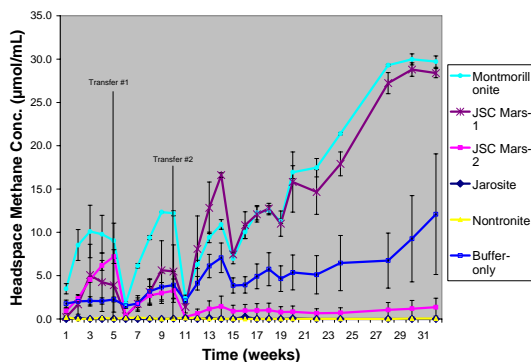
Figure 3: Methane production by *M. wolfeii* on various Mars-relevant geochemical substrates.

Discussion: The results presented here indicate that methanogens can obtain necessary micronutrients from materials present on Mars. Subsequent, smaller investigations have supported this conclusion. These results also prompted us to inquire why two similar clay substrates such as nontronite and montmorillonite showed such contrasting results. The major difference between the clays is the high Fe^{3+} content of nontronite. It was first thought that the Fe^{3+} might be oxidizing the CH_4, but work we have done to test this idea has suggested otherwise. An investigation has now been initiated to determine if the methanogens are preferentially metabolizing the Fe^{3+} in the nontronite. Visual comparison of microenvironments and initial analysis of the liquid phases present in the substrate tubes indicate that reduction of Fe^{3+} may be occurring, though XRD and magnetic analysis of the solid phase has not yet been completed. It is thought that the dark layers shown in the below (Figs. 4, 5) are magnetite, a mineral containing both ferrous and ferric iron phases.

Figure 4: Balch-tube microenvironments containing nontronite and bicarbonate buffer. This picture was taken early in a follow-up study. The six tubes on the left showing discoloration contain methanogenic species, while the two control tubes on the right are identical except for their lack of microorganisms.
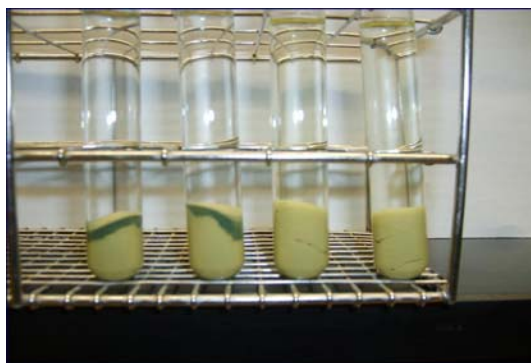

Figure 5: A close-up of the aforementioned tubes. The two tubes on the left contain bicarbonate buffer, nontronite, and *M. barkeri*. The two tubes on the right contain bicarbonate buffer and nontronite, but they were not inoculated with any methanogens.

Experiments utilizing alternate electron sources known to occur on Mars are ongoing in our laboratory, as are experiments involving methanogens with Mars-like optimal growth temperatures.

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FUTURE IN SITU METHANE AND RELATED TRACE GAS AND ISOTOPE MEASUREMENTS WITH THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE OF THE 2011 MARS SCIENCE LABORATORY (MSL).

P. R. Mahaffy[1], C. R. Webster[2], M. Cabane[3], P. Coll[3], and S. K. Atreya[4], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA (Paul.R.Mahaffy@nasa.gov), [2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, [3]LATMOS and University of Paris VI, France, [4]University of Paris VII, France, and [5]University of Michigan, Ann Arbor, Michigan 48109.

Introduction: The determination of the mechanism of the recently established Mars methane production [1,2,3], be it biotic or abiotic, may be approached, as it is in analogous terrestrial research, [4,5] by evaluation of patterns revealed in other trace gases and in isotopes of carbon, hydrogen, and other light elements. These are likely to precede the more difficult direct search for microbial life or for perhaps deep chemical environments that produce abiotic methane through serpentinization reaction of olivine with H_2O and CO_2. Orbital approaches to measurement of both methane and other trace gases in the atmosphere of Mars are presently under detailed study for implementation in the 2016 launch opportunity. Complementing the orbital sensing are surface measurements, such as the suite of analytical tools provided by the 2011 Mars Science Laboratory (MSL). These provide the ability to not only sample the atmosphere, but also to analyze the chemical and isotopic composition of the near surface soils and rocks that may or may not be the source of the methane. We describe the contribution expected from MSL and its Sample Analysis at Mars (SAM) instrument suite not only to detect methane, but to also carry out other measurements related to the mechanism of methane production.

MSL Science Objectives: The 2011 Mars Science Laboratory (MSL) is designed to quantitatively assess the region of its selected landing site as a potential habitat for present or past life. MSL's increased payload allocation enables a more comprehensive measurement capability that any other Mars rover, to date. Its science goals are (1) to assess past or present biological potential of a target environment, (2) to characterize geology and geochemistry, and (3) to investigate planetary processes that influence habitability.

SAM Measurement Capability: The Sample Analysis at Mars (SAM) Suite consists of a gas chromatograph (GC), a mass spectrometer (MS), and a tunable laser spectrometer (TLS) and supporting sample manipulation and gas processing systems. SAM is designed to carry out a sensitive search for organic molecules and implement chemical and isotopic analysis of volatiles while MSL contact and remote surface and subsurface survey instruments establish geological context. SAM is designed to analyze either the atmospheric composition or gases extracted from solid phase samples such as rocks and fines. One of the core SAM experiment sequences heats a small powdered sample of a Mars rock or soil from ambient to ~1300 K in a controlled manner while continuously monitoring evolved gases. This is followed by GCMS analysis of released organics that have been trapped out of the gas stream. The general SAM chemical survey of volatiles is enhanced by a specific search with a solvent extraction and chemical derivatization for molecular classes that may be relevant to life such as amino acids and nucleobases.

Methane and Relevant Isotope and Trace Gas Measurements: The SAM Tunable Laser Spectrometer (TLS) [6] implements the sensitive search for atmospheric methane and its carbon isotope. Methane is processed and enriched for the TLS measurements in the SAM gas processing system. Temporal variations may be studied over the course of the two-year landed mission. In addition to atmospheric diurnal and seasonal variations, the most significant related measurements that may contribute to an understanding of the source of the methane are simultaneous measurements of the D/H ratio in water and measurements of other trace hydrocarbons either in the atmosphere or in surface rock and soil samples. Methane and its carbon isotope produced by pyrolysis will also be measured by the TLS. The SAM combustion experiment may determine the source carbon isotopic composition by conversion of rock or soil macromolecular carbon into CO_2.

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[1] Formisano V. et al. (2004) Science 306, 1758-1761. [2] Krasnopolsky V. A. (2005) Icarus, 172, 537-547. [3] Mumma M. J. et al., (2009) Science, 323, 1041-1045. [4] Sherwood Lollar B. et al., (2006) Chemical Geology, 226, 328-339. [5] Onstott T. C. et al., (2006) Astrobiology, 6, 377-395. [6] Webster C. R. (2006) Appl. Optics 44, 1226-1235.

MEASURING METHANE AND ITS ISOTOPIC RATIOS $^{13}C/^{12}C$ AND D/H WITH THE TUNABLE LASER SPECTROMETER (TLS) ON THE 2011 MARS SCIENCE LABORATORY (MSL) MISSION.

C. R. Webster[1] and P. R. Mahaffy[2], [1]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, [2]NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771.

Introduction: The Tunable Laser Spectrometer (TLS) in one of three instruments (QMS, GC, TLS) that make up the Sample Analysis at Mars (SAM) analytical chemistry lab [1] on NASA's 2011 Mars Science Laboratory (MSL) mission (Fig. 1). Leveraging off the SAM gas processing capability, TLS has unprecedented sensitivity for measuring methane, water, and carbon dioxide abundances in both the Martian atmosphere and evolved from heated soil samples.

The TLS Instrument in SAM: TLS uses two tunable laser sources, an interband cascade (IC) laser at 3.27 µm made at JPL, and a tunable diode laser (TDL) at 2.8 µm made by Nanoplus, Germany, specifically for this Mars mission (see Fig. 2).

Figure 1: TLS (cylindrical spectrometer across the lower left) is mounted in the SAM structure).

Figure 2: The two laser sources with triple-lens collimators are mounted to the 4-inch square laser plate ready for insertion into the spectrometer.

Gas Abundances: With SAM pre-concentration, TLS has capability to determine atmospheric methane abundance to a lower limit of ~1 part-per-trillion. In addition, TLS can detect both carbon dioxide and water in soil or rocks to 10^{-10} weight%.

Isotope Ratio Determinations:
TLS will measure the $^{13}C/^{12}C$ and D/H isotope ratios in methane; the $^{13}C/^{12}C$ and $^{16}O/^{17}O/^{18}O$ isotope ratios in CO_2; and the D/H and $^{16}O/^{17}O/^{18}O$ isotope ratios in water (see [2] for Earth water isotope measurements]. While formal instrument requirements specify isotope ratio capability to 10 per mil (0.1%), flight instrument environmental testing shows that we can expect determination of these isotope ratios to a few per mil.

Spectral Regions:
The spectral region chosen for the TLS methane measurements [3] is shown in Figure 3 below, accessing a group of three strong lines of R(4) and four strong carbon-13 methane lines. A weak CH_3D line rests right before the main parent methane line. Temperature settings of the Nanoplus laser can be changed to sequentially access two regions for carbon dioxide and water. Although the water region has some interferences from carbon dioxide, first of all SAM can scrub the gas out, and then the water isotope ratio measurements will be made on evolved water from solid samples, of which we expect large relative amounts.
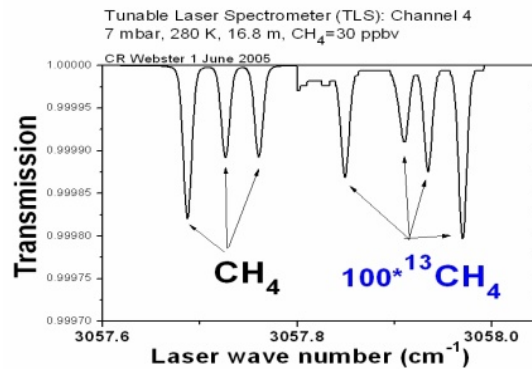
The instrument and test data results will be described in context with the expected abundances [4] on Mars.

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[2] Webster, C.R. and Heymsfield (2003) A.J., *Science 302*, 1742-1745.
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[4] Mumma, M.J. et al., (2009) *Science 323,* 1041-1045; Formisano, V. et al. (2004), *Science 306,* 1758; Krasnopolsky, V. (2007) *Icarus 190,* 93.

STUDYING METHANE AND OTHER TRACE SPECIES IN THE MARS ATMOSPHERE USING A SOIR INSTRUMENT.

R. Drummond[1], A.C. Vandaele[1], F. Daerden[1], E. Neefs[1], A. Mahieux[1], V. Wilquet[1], F. Montmessin[2, 3], J-L. Bertaux[2], E. Marcq[2]
[1]Belgian Institute for Space Aeronomy, 3 Ringlaan, 1180 Brussels, Belgium; rachel.drummond@aeronomie.be, [2]LATMOS, 91371 Verrières-le-Buisson, France, [3]IPSL, Université UVSQ, Guyancourt, France

Introduction: SOIR (Solar Occultation InfraRed spectrometer) is currently part of the SPICAV/SOIR instrument[1] on board the Venus Express orbiter (VEX). SOIR, an Echelle infrared spectrometer using an acousto-optic tunable filter (AOTF) for the order selection, is probing the atmosphere by solar occultation, operating between 2.2 and 4.3 μm, with a resolution of 0.15 cm^{-1}. This spectral range is suitable for the detection of several key components of planetary atmospheres, including H_2O and its isotopologue HDO, CH_4 and other trace species. The SOIR instrument was designed to have a minimum of moving parts; and to be light and compact. The AOTF allows a narrow range of wavelengths to pass, according to the radio frequency applied to the TeO_2 crystal; this selects the order. The advantage of the AOTF is that different orders can be observed quickly and easily during one occultation. To obtain a compact optical scheme, a Littrow configuration was implemented in which the usual collimating and imaging lenses are merged into a single off-axis parabolic mirror. The light is diffracted on the echelle grating, where orders overlap and addition occurs, and finally is recorded by the detector. The detector is 320x256 pixels and (for the VEX-SOIR version) is cooled to 88K during an occultation measurement, to maximise the signal to noise ratio.

Measurement technique: The occultation technique employed by SOIR is based on comparing observations of a light source performed outside and through an absorptive medium (the atmosphere of a planet) in order to simultaneously obtain a reference signal and the relative light intensity loss caused by the presence of absorbent molecular species interfering with the beam. The "absorptive" term actually refers to the loss of light intensity either by scattering (Rayleigh, aerosols) or by absorption (usually molecular). One can determine the amount of light that is transmitted by a planetary atmosphere (Venus' or Mars') as a function of altitude and wavelength.

SOIR at Mars: VEX has been in orbit around Venus since April 2006. To date SOIR has carried out over 560 measurements (219 occultations and 345 calibration measurements). Pre-launch and in-orbit performance analyses allow us to predict what SOIR would be capable of at Mars.

SOIR spectra of solar occultations through the Martian atmosphere have been simulated with ASIMUT, a LBL radiative transfer code also used for the retrieval of vertical profiles of atmospheric

constituents of Venus[2,3]. The code takes into account the curvature of the atmosphere, temperature and pressure vertical profiles as well as those of the atmospheric species, but also the instrument function and the overlapping of the diffraction orders of the echelle grating. Figure 1 shows the absorption line intensities for methane in red over a simulated SOIR spectrum for a typical Martian atmosphere in blue, with the yellow band being the noise level. We can see that the methane would be detectable. We will also present the detection limits of species that could be studied using a SOIR spectrometer making solar
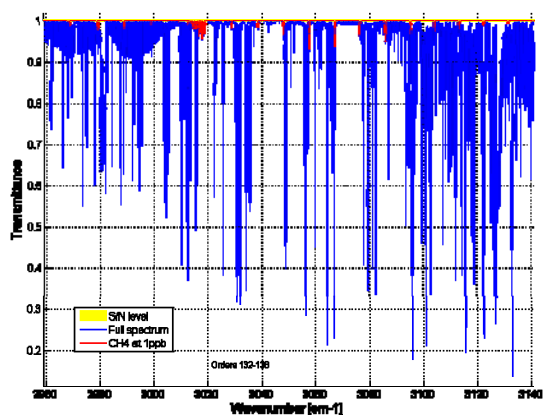
occultation measurements in Mars orbit.

Figure 1 Methane at 1ppb over an atmospheric spectrum; focusing on the 3.3μm methane feature

SOIR in Nadir Mode (TGM): This paper will present SOIR, the instrument and its capabilities. A future version of SOIR could be adapted to perform nadir measurements with a better signal to noise ratio. We will therefore discuss the instrument modifications that would need to be made in order to perform this trace gas mapping (TGM). The impact on mass and performance will be discussed.

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[1] J. L. Bertaux, et al.,(2007), *Planetary and Space Science 55* (12), 1673-1700. [2] A. C. Vandaele, et al., (2008), *J. Geophys. Res. 113, E00B23*, doi: 10.1029/ 2008JE003140. [3] J.-L. Bertaux, et al., (2007), *Nature 450* (29 November), 646-649, doi:10.1038/nature05974

A NEW MISSION CONCEPT: THE SEARCH FOR ATMOSPHERIC TRACE GASES IN THE MARS ATMOSPHERE.

Richard W Zurek[1] and Augustin Chicarro[2], [1]Jet Propulsion Laboratory, California Institute of Technology (JPL MS 264-535, 4800 Oak Grove Drive, Pasadena, CA 91109; rzurek@jpl.nasa.gov), [2]Exploration Programme, European Space Agency (achicarr@rssd.esa.int).

Introduction: Measurements from Earth-based telescopes and from Mars orbit indicate the presence and rapid variation (months to a few years) of methane in the Mars atmosphere [1,2,3]. This is inconsistent with the present understanding of the photochemical lifetime of methane there, unless there is an active source on/in the surface that replenishes methane *and* there is something other than the gas-phase photochemistry of the trace species known to exist. This implies both an active source and possibly heterogeneous chemical reactions on the ice and dust in the atmosphere.

The nature of the subsurface source is of particular interest as it may be the results of biogenic or geochemical processes. If the latter, those processes may still provide an energy source that biota could tap. Even if unrelated to life, the methane observations indicate photo- or electro-chemical processes in the atmosphere that should affect more than just methane. What is needed is a detailed characterization of the atmospheric inventory of trace gases, of potential chemical processing, and thus of the roles of the major gases and aerosols in the Mars atmosphere.

Mission Definition Activity: Recently, ESA and NASA formed a Joint Instrument Definition Team (JIDT) to consider what might be done from an orbital platform possibly launched in 2016 to advance our understanding of trace gases in the Mars atmosphere. This group's work was within the framework of discussions of a joint mission or missions to Mars in the next decade. This presentation will report highlights of the ongoing discussions regarding possible science mission objectives and measurement capabilities needed to achieve them. Three scientific goals emerged:

- Detection of broad suites of trace gases and their isotopes, some possibly present in concentrations as low as a few parts per trillion;
- Mapping of a few key species (e.g., methane itself) in order to characterize their variability in space and time and to identify local sources, if they exist;
- Characterization of the atmospheric state—temperature, water vapor, dust and ice loading—and atmospheric transport, both to assist the localization of sources and to detect changes due to possible heterogeneous photochemical processes.

The JIDT survey of the required measurement capabilities indicated that instruments exist or could be reasonably built that could fulfill these requirements within the possible envelope of payload and spacecraft resources.

Given current observations and theoretical understanding, comprehensive exploration of atmospheric trace gases also requires characterization of their variation with time of day and with season. Coverage over much of the planet is also required in a way that could separate temporal and spatial variation.

To separate contributions of transport and photochemistry requires representative time of day coverage and full seasonal coverage, as variations on time scales of months have been suggested by the present observations of methane and knowledge of some of the key photochemical players, such as water vapor. Thus, the JIDT concluded that the science phase of the mission should last at least one Mars year.

The discussion by the JIDT of possible approaches to mission choices of orbit period and altitude, precession and inclination will be presented. More details may be known at the time of the meeting regarding the possibility of such a joint ESA-NASA orbiter mission launched in 2016 to study trace gases in the atmosphere of Mars.

References: Use the brief numbered style common in many abstracts, e.g., [1], [2], etc. References should then appear in numerical order in the reference list, and should use the following abbreviated style:

[1] V. Formisano et al. (2004) *Science, 306,* 1758-1761.

[2] V. A. Krasnopolsky, J. P. Maillard and T. C. Owen (2004) *Icarus, 172*, 537-47.

[3] M. J. Mumma et al. (2009) *Science, 323*, 1041-1045.

Determination of the surface concentrations of methane on Mars with MOMA. H. Steininger[1],

[1] Max Planck Institute for solar system research, Katlenburg-Lindau, Germany, (steininger@mps.mpg.de / Fax: +49-5556-979240)

Introduction: The Mars Organic Molecule Analyser (MOMA), a combined laser desorption – mass spectrometer and gas chromatograph – mass spectrometer, on board the European ESA ExoMars mission to Mars will be one of the few opportunities for the ground based measurement of methane on Mars in the next decade. The average concentration of methane derived from satellite based measurements is 14±5 ppbv [1]. Seasonal changes indicate a massive source for methane and therefore a much higher concentrations at the source of the methane[2]. For successful detection the instrument should be capable to reach the lower concentration limit of 9 ppbv. Although MOMA is designed for heavier organic molecules than methane to measure the methane concentration in near surface atmosphere is a secondary goal of the instrument.

Instrument limitations: The objective of MOMA implies some limitations for the detection of methane. Beginning with the sample intake of the MOMA instrument which includes the pyrolysis in 0.5 ccm oven or a laser desorption. An atmospheric sampling is possible, but only from the atmosphere trapped in an empty oven. This limits the sample size to 0.5 ccm. The GC is capable to separate methane from the other components in Martian atmosphere and therefore a pure sample of methane in helium would reach the MS. The detection level of the MS is not sufficient to detect low ppb levels of methane within the 0.5 ccm sample. Additionally the ion trap MS will use Martian atmosphere as collision gas in the trap, making a detection of molecules lighter than CO_2 and N_2, (especially methane) very difficult due to the ionization method and the mass cut off of the ion trap.

Hardware development: To overcome the limitations of the instrument several changes in the hardware are under investigation. The low methane concentrations make it necessary to enrich it before the introduction in the gas chromatograph – mass spectrometer. An additional pump could collect a larger sample of Martian atmosphere and extract the methane by an adsorption trap. The selection of a trap material sufficiently selective for methane over nitrogen and carbon dioxide is a critical task in this undertaking. To enable the detection of methane in the ion trap, the collision gas in the trap can be substituted by helium or the carbon dioxide can be eliminated from the trap by electronically modifying the radiofrequency used for trapping.

Conclusion: The above mentioned hardware changes are under evaluation and together with a lower boundary for the expected amount of methane we will be able to determine if MOMA is capable to measure trace amounts of methane on Mars.

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[1] Geminale A. et al. (2008) *Planet. & Space Sci., 56,* 1194–1203. [2] Mumma M. J. et al. (2009) Science, *323,* 1041–1045.

USING INFRARED LASER HETERODYNE RADIOMETRY TO SEARCH FOR METHANE ON MARS.

R. L. Passmore[1], N. E. Bowles[1], D. Weidmann[2] and K. M. Smith[2].
[1]Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford. OX1 3PU. U.K. E-mail: passmore@atm.ox.ac.uk. [2]Space Science & Technology Department, STFC Rutherford Appleton Laboratory, Harwell Science & Innovation Campus, Didcot, Oxfordshire. OX11 0QX. U.K.

Introduction: Methane has been detected in the atmosphere of Mars by several research teams in the last few years. Ground-based observations[1][2] and space-based instruments (e.g. the Planetary Fourier Transform spectrometer on Mars Express[3]) have reported low levels of methane gas (approximately 10 ppb) in the Martian atmosphere. Methane detection is important as its presence could imply a biological origin, and Martian methane sources are still unknown. However, current methane concentration measurements are at instruments' lower limits of detection.

The viability of remote sensing using infrared laser heterodyne radiometry (LHR) to detect methane in the Martian atmosphere is investigated. The LHR technique allows high spectral resolution (greater than 0.001 cm^{-1}) measurements over a narrow spectral range (~ 10 cm^{-1}) when a quantum cascade laser is used as local oscillator. The advantages of such an instrument, including its compact lightweight design, over current remote sensing spectral instruments are reviewed.

The Laser Heterodyne Radiometer: Laser heterodyne radiometers have been used extensively, and with much success, for atmospheric studies, such as work on stratospheric ozone[4], mainly because of their ability to make measurements with an ultrahigh spectral resolution (greater than 0.001 cm^{-1}).

A carefully selected specific high resolution microwindow provides as much information as a medium resolution radiometer covering a broad spectral range[5]. This major advantage favours the development of a small and lightweight LHR instrument over the current large and heavy Fourier transform spectrometers (FTS). FTS instruments require large optical path differences to achieve a high spectral resolution, which result in their large physical size and mass.

At the heart of the state of the art infrared LHR is the use of a Quantum Cascade Laser (QCL) as the local oscillator. QCLs are an ideal local oscillator for this instrument as they provide the necessary optical power and have spectral purity in the kHz to MHz range[5]. They have the advantage of continuous frequency tuning over a specific spectral window that can be precisely tailored to specifications. They also have the advantage of being extremely compact, robust and reliable devices which make them ideal candidates for flight and satellite deployment.

References: [1] Krasnopolsky et al. (2004) *Icarus*, 172, 537-547. [2] Mumma et al. (2009) *Science*, 323, 1041. [3] Formisano et al. (2004) *Science*, 306, 1758-1761. [4] Weidmann et al. (2007c) *Applied Optics*, 46, 7162-7171. [5] Weidmann et al. (2007b) *Review of Scientific Instruments*, 78, 73107.

ROBOTIC RIGID VACUUM AIRSHIP FOR EXPLORATION OF MARS.

S. Pahari, Politecnico di Milano, Departimento di Chemica, 32 Piazza Leonardo da Vinci, 20133 Milano, ITALY, sougatapahari@gmail.com

Introduction: Land-based exploratory vehicles like the Spirit and the Opportunity have typical navigation range of less than a hundred metres a day and so have to be deployed close to the targets of interest. ESA's Mars Express is being designed to further extend the range. There remain no doubts or surprises that unmanned aerial vehicles would far surpass the range, efficiency speed and flexibility of their land-based counterparts. Airplanes and rotorcrafts have a relatively low operational life and being fast moving will pose restrictions to study in addition to requiring a solar-collector area of 7.5 times greater than it would be required on Earth to fly the same payload [1]. The Lighter Than Air (LTA) systems are best suited for such tasks. They are slow-moving, have a very large surface area for photovoltaic cells, can allow long-range as well as close-up observations, they can carry their payload of instruments and equipments and deploy them over vast distances and are highly efficient [2]. In addition they will enable us to get direct samples of the atmosphere at various altitudes [3] in addition to studying the complex atmospheric phenomenon like the jet streams.

Using the general concept of LTA systems that we use here on Earth will prove cumbersome on Mars, for the same payload, a volume 200 times greater is required on Mars, in spite of having only a third of Earth's gravity [1]. Such a huge volume will paralyze operations and reach of the vehicle. A vacuum shell airship might prove feasible. In such an airship partial vacuum is created within the rigid structure instead of filling it with a buoyant lifting gas. It was first envisaged by Francesco de Lana in 1670 [4]. Building such an airship is impossible in the thick and heavy atmosphere on Earth as the pressure difference would be as great as 10,000 kg/m², but on Mars, the difference would be as little as 70 kg/m² [1].

If we opt for the conventional propulsion system of propeller blades the operation will prove to be relatively inefficient due to the low Reynold's number of the Martian atmosphere [1].

In this paper we present the conceptual design of a solar-powered rigid vacuum airship capable of traversing to any location on Mars and deploying instrumentation for in-situ sampling and analysis of atmosphere, soil, rocks and ice-caps. We also present a novel system of navigation by C.G. vectoring. To navigate the airship will gain in altitude varying its buoyancy (by varying the vacuum pressure within) and Glide to a desired location by calculated positioning of its C.G. and the wing assembly. We also present operation strategies for the craft and the specific instrumentation required we consider optimum for detection and study of the methane clouds on Mars.

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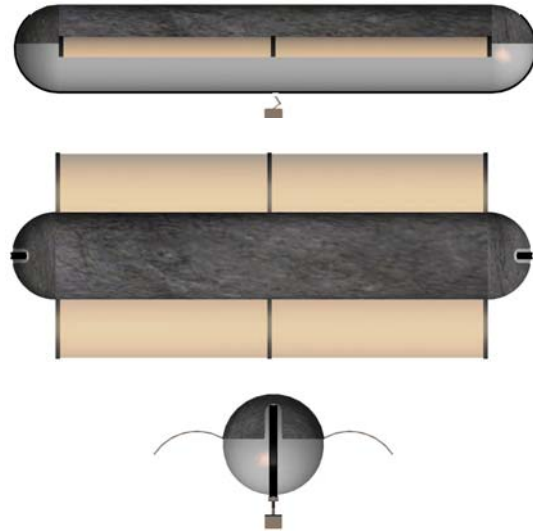
Right, Top and Front view respectively of the rigid vacuum Airship.

DETECTING AND CHARACTERIZING MARTIAN DUST USING SPECTROPOLARIMETER SPEX

D. M. Stam[1] (d.m.stam@sron.nl), J. M. Smit[1], F. Snik[2], C. U. Keller[2], and the other members of the SPEX consortium[3], [1]SRON Netherlands Institute for Space Research, Sorbonnelaan 2, 3584 CA Utrecht, [2]Astronomical Institute Utrecht University, [3.]TNO Science & Industry, Astron, Dutch Space, Cosine, Mecon, all in the Netherlands.

Introduction: Dust is ubiquitous in the Martian atmosphere. Dust particles play an important role in quantifying and understanding Mars' methane budget: 1. dust influences the retrieval of methane column densities, because the particles scatter and absorb radiation, and hence change the shapes of gaseous absorption bands in Mars spectra; 2. dust particles provide surfaces for chemical reactions, thus serving as possible sinks of methane [1]; and 3. electrical discharges in dust storms change the atmospheres' chemical composition and hence indirectly affect methane [2]. Clearly, detecting dust, measuring its optical thickness, and characterizing its microphysical properties (size, composition, shape) of dust particles and their spatial and temporal distribution should be an intrinsic part of the study of methane on Mars. Here, we present SPEX, our Spectropolarimeter for Planetary EXploration, a compact and robust novel instrument for remote-sensing of atmospheric particles, such as dust, from orbit.

Spectropolarimetry: The detection and characterization of dust particles are usually done using flux measurements of reflected sunlight and/or the planet's thermal radiation, at several wavelengths λ and a number of viewing angles. This flux, however, is very insensitive to particle microphysics; to derive e.g. the composition, assumptions on particle sizes and shapes have to be made. It has been shown [see e.g. 3] that to accurately derive the microphysical properties of atmospheric particles, one should measure the degree of polarization P of the reflected sunlight, preferably at several wavelengths, and at a number of scattering angles. The latter gives the polarized phase function, the shape of which is very sensitive to particle microphysics. In particular, the combination of flux and polarization observations is a strong tool for deriving information on both the number density of particles and their microphysical properties.

SPEX (Spectropolarimeter for Planetary EXploration): Several space missions, for remote-sensing of the Earth or other planets, have (had) instruments with polarimetric capabilities, usually spectrometers with 2 or sometimes 3 polarizers in their filter wheels (the fluxes measured through the polarizers are then combined to derive P). Unfortunately, these polarimeters usually cover limited spectral ranges with low (broadband) resolution. In addition, their polarimetric accuracy is usually too low to take full advantage of polarimetry, because the separate flux measurements are obtained at different times, and through different optical components.
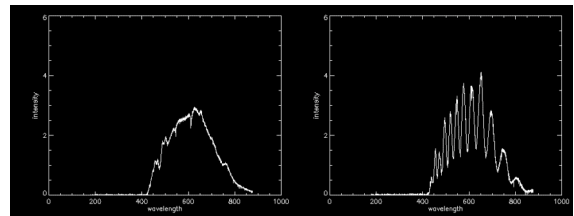

Fig. 1: Flux measurements with a laboratory set-up to illustrate SPEX' novel polarimetric method (see Eq.1). On the left: F_{mod} for P=0. On the right: F_{mod} for $P{\approx}0.5$.

SPEX is designed to simultaneously measure the flux F and degree of polarization P of sunlight that is reflected by a planet from 0.4 to 0.8 μm with a spectral resolution of 2 nm (F) to 20 nm (P). To achieve this, SPEX uses a novel polarimetric method that is based on a carefully selected combination of birefringent crystals [4] that transforms an incoming flux spectrum into two spectra, each of which is spectrally modulated with P:

$$F_{mod}(\lambda)= 0.5F(\lambda)[1\pm P(\lambda)\cos(2\chi(\lambda)+2\pi\delta(\lambda)/\lambda)], \quad (1)$$

with F_{mod} the observable flux, χ the direction of polarization, and δ the retardance of the birefringent crystals. Adding the 2 flux spectra gives flux F, while P is derived from the modulation (see Fig. 1).

In its current design, SPEX measures F_{mod} through fixed apertures along the orbiter's track (see Fig. 2): 7 in the nadir direction and 2 towards the limbs (for the detection and characterization of ice clouds). This version of SPEX is small (~5 kg), without moving parts, and requires little power (for the detector). A SPEX demonstration model is being constructed.
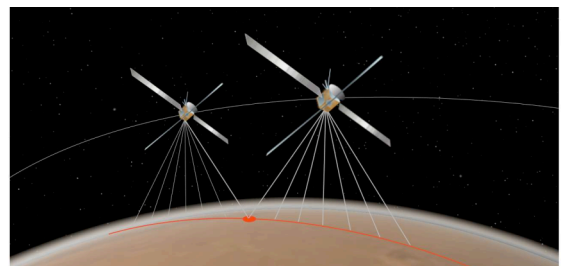

Figure 2: SPEX' observing method. A region on the planet is observed from a range of angles as the orbiter passes over it (the 2 limb viewers are not shown here).

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POSSIBLE INFLUENCES OF AEROSOL LOADING ON THE MEASURED COLUMNS OF MARTIAN ATMOSPHERIC CONSTITUENTS INCLUDING METHANE.

C.Muller , F.Daerden and D. Moreau, Belgian Institute for Space Aeronomy (IASB-BIRA), avenue circulaire, 3, B-1180 Brussels, Belgium Christian.Muller@busoc.be

Introduction:

The Martian atmosphere shows a variability in atmospheric parameters which has no equivalent on earth, the surface temperature can easily be inferior to the condensation temperature of the main gas, carbon dioxide and thus strong variations of the columns of carbon dioxide and water vapour are expected on Mars. For photochemical reasons, ozone has shown also since Mariner 9 important latitudinal and temporal variations, these have been confirmed by Mars-Express. More surprising are the observed spatial variations of methane observed by PFS on Mars-Express and telescopic observations. On earth, well characterized methane sources as oil extraction sites show an almost negligible methane enhancement due to rapid transport and long life-time. The same rationales should apply to Mars even more and except if one accepts an exceptional local production process and a shortening of the life time due to a specific Martian chemistry no explanation for these observations has ever been presented.

Martian aerosols influence :

It is thus proposed to review the properties of Martian dust as influencing the wavelengths where these molecules are observed. Especially in the infrared, most estimates of dust effects are made with small particles with negligible absorptions. Absorbing layers would change entirely the perspective by masking the lower part of the atmosphere and decreasing thus the column of atmospheric gases. If these masks were not spatially uniform, they would result in spatial variations of the columns which could lead to wrong mixing ratios if compared to a Mars CO2 model.

Preliminary simulations have been made using the MODTRAN desert aerosol as an analogue (this is based on a Libyan sand containing a percentage of iron oxide much lower than the one determined in the MER mission. These simulations correspond to the preparatory studies for the UVIS UV-visible monitor which was part of the EXOMARS payload. It is clear that an enhancement of dust on Mars would produce a broad absorption at 3 micrometer and thus decrease the signal/noise ratio of the observations of minor constituents.
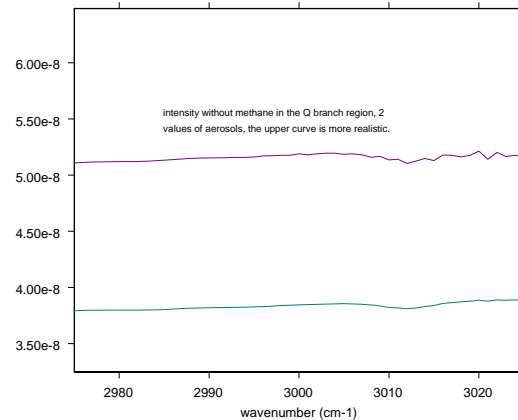

Fig 1. : MODTRAN nadir signal intensity without methane, the intensity unit corresponds to irradiance in Watts/cm2 for an interval of 1 cm-1. The lower curve is the curve with aerosols exaggerated by a factor of 10, the upper one corresponds roughly to "Pathfinder" data obtained in the visible.

Conclusions for Martian methane observations :

The different formation mechanisms for aerosols have to be studied to know their nature and thus determine their radiative transfer properties. The worst case would be particles coated with an organic absorber, they would form a selectively absorbing layer which would hide methane .lower atmospheric absorptions. Oxidation of methane by producing polymerized formaldehyde on dust particles might be a source of such particles.

Strategies to avoid the problem will be discussed: multiple wavelengths, derivation of the atmospheric model from the data, precise radiometric calibration and simultaneous use of limb observation.

All of them require a special instrument characterization and calibration plan comparable to the one required for the most precise earth observation instruments.