Atmospheric Chemistry Suite: Science Overview

"Conventional" chemistry
Investigations B3, C1

Active release
Investigations A1, A2, A3, B2

Dust chemistry
Investigation B1

Methane loss by heterogeneous chemistry

Methane loss by electrochemistry

Dust storms

Volcano, Hot spot

Constraining Mars photochemistry and activity

Fast chemical coupling

Never detected

Measured

Airglow measured

biotic activity hydrothermalism
TECHNOLOGY OBJECTIVE
- Entry, Descent, and Landing (EDL) of a payload on the surface of Mars.

2016

SCIENTIFIC OBJECTIVE
- To study Martian atmospheric trace gases and their sources, possible signature of geophysical or biological activity.

Provide data relay services for landed missions until 2022.
**ExoMars Scientific Objectives**

- To search for signs of past and present life on Mars
- To investigate the water/geochemical environment as a function of depth in the shallow subsurface
- To investigate Martian atmospheric trace gases and their sources.

**Trace Gas Orbiter Objectives**

- Detection of a broad suite of atmospheric trace gases, **possible signature of geophysical/biological activity on Mars**
- Characterization of their spatial and temporal variation
- Localization of the sources of key trace gases
What geophysical gases should we expect?

On the Earth, the principal components of volcanic gases are water vapor (H\textsubscript{2}O), carbon dioxide (CO\textsubscript{2}), sulfur either as sulfur dioxide (SO\textsubscript{2}) (high-temperature volcanic gases) or hydrogen sulfide (H\textsubscript{2}S) (low-temperature volcanic gases), nitrogen, argon, helium, neon, CH\textsubscript{4}, CO and H\textsubscript{2}.
List of TGO high priority target species

H2O, HO2, H2O2, NO2, N2O, CH4, C2H2, C2H4, C2H6, H2CO, HCN, H2S, OCS, SO2, HCl, CO, O3
Most chemical species released by geophysical activity have “short” chemical lifetimes:

- CH4 300 yrs
- SO2 1-2 years
- CO 3 years

While CO2 and H2O already exist in significant quantities (detecting fluctuations is difficult and ambiguous wrt. other potential processes)

The search for geochemical gases can only trace very recent or ongoing activities
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Is there surface hints of current/recent geophysical activity on Mars?

- Geomorphological evidences of recent volcanic activity (106-7 yrs)
- Sulfate deposits in the North polar region (Langevin et al., 2005; Fishbaugh et al., 2007)
- However, Themis IR mapper sees no hot spot (Christensensen, 2003)
Is there surface hints of current/recent geophysical activity on Mars?

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# TGO science instruments

## NOMAD
High resolution occultation and nadir spectrometers

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Wavelength Range (µm)</th>
<th>Resolving Power (λ/Δλ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVIS</td>
<td>0.20 – 0.65</td>
<td>~ 250</td>
</tr>
<tr>
<td>IR</td>
<td>2.3 – 3.8</td>
<td>~ 10,000</td>
</tr>
<tr>
<td>IR</td>
<td>2.3 – 4.3</td>
<td>~ 20,000</td>
</tr>
</tbody>
</table>

## CaSSIS
High-resolution camera

- Atmospheric composition
  - \(CH_4, O_3,\) trace species, isotopes
  - Dust, clouds, P&T profiles

## ACS
Suite of 3 high-resolution spectrometers

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Wavelength Range (µm)</th>
<th>Resolving Power (λ/Δλ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near IR</td>
<td>0.7 – 1.7</td>
<td>~ 20,000</td>
</tr>
<tr>
<td>IR (Fourier, 2 – 25 µm)</td>
<td>~ 4000 (SO)/500 (N)</td>
<td></td>
</tr>
<tr>
<td>Mid IR</td>
<td>2.2 – 4.5</td>
<td>~ 50,000</td>
</tr>
</tbody>
</table>

## FREND
Collimated neutron detector

- Mapping of subsurface water

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All resolving power figures \(\lambda/\Delta\lambda\) are calculated at mid-range.
The ACS-NOMAD Complementarity
ACS: Major Science themes

- **“Breakthrough” Science**
  - with MIR channel Solar Occultations
  - Trace Gas detection with ppt sensitivity or/and revisit upper limits (may probably set an “all time” reference for future exploration missions)

- **“Novel” Science**
  - with all channels in Nadir/Occultation
  - First mapping of D/H ratio
    new information on water reservoirs and their history, cloud processes
  - Oxidant species
    HOx family (e.g. H2O2, OH, HO2) barely characterized on Mars, only reactants (O3)

- **“Climatological” Science**
  - with TIRVIM and Near-IR in nadir
  - Mapping of meteorological fields
    temperature, dust / ice aerosols, water vapor
The ACS-NOMAD Complementarity

O3, SO2, *NO
CH4, H2O, HO2, HDO, HF, HCL, SO2 CO2 + isotopes, etc.
CO2, H2O2 dust, water ice
ACS-NOMAD: synchronizing the approaches?

• Two comparable and highly capable instruments on the same platform
• This mission may set a new standard for Mars atmosphere composition. For this reason, it is probably better to have one single and loud voice
• Complementarity (spectral and thus scientific) between the two instruments is obvious: may lead to common effort threads (oxidants + O3)
• ExoMars TGO will feel the pressure of a community expecting confirmation/contradiction of CH4 existence
• Two instruments saying the same thing at the same time is the safest way to go to make results believable by our community
• Corrdinate announcement for (non)detection of any “hot” trace gas species (by the ExoMars Project Scientist)
• Scientific coordination between the two instruments should be a major task of ExoMars Project
Suggestions for Science Management Plan for ACS

• Having data pipeline ready by Mars Orbit Insertion will be critical for a prompt delivery of early results (upper limits or detection of trace species)

• We should define a priority ordering and a elaborate a schedule for **building and testing data pipelines** (example of MAVEN: data pipeline ready at launch, counter-example of SPICAM-UV: pipeline insufficiently mature, first conclusion proved to be wrong)

Will the commissioning phase be useful in that regard; i.e. help refine instrument characterization (any sun stare planned during cruise?)
Trace species visible in the IR

“Hydrocarbons window” (CH4, C2H6, CH3OH, C2H4, etc.)

- CO2: Carbon dioxide 95%
- C2H6: Ethane 20 ppb
- HCl: Hydrogen Chloride 100 ppb
- H2O: Water 100 ppm
- CH4: Methane 50 ppb

Frequency in Mars rest frame [cm⁻¹]

“Water D/H window”

- HDO: Deuterated water Considering D/H=5
- H2O: Water 100 ppm
- CO2: Carbon dioxide 95%

Frequency in Mars rest frame [cm⁻¹]
ACS observations in Solar Occultations

- TGO spacecraft
- Orbit
- Sun
- Line of sight
- Normalized absorption spectra
  - CO₂: Carbon dioxide 95%
  - C₂H₆: Ethane 20 ppb
  - HCl: Hydrogen Chloride 100 ppb
  - H₂O: Water 100 ppm
  - CH₄: Methane 50 ppb
- Frequency in Mars rest frame [cm⁻¹]
Constraining Mars photochemistry and activity.
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Potential (yet to be identified) chemistry

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Constraining Mars photochemistry and activity

$\text{H}_2\text{O}$ → $\text{NO}_2$ → $\text{O}_3$ → $\text{O}_3$

$\text{CO}_2$ → $\text{OH}$ → $\text{HO}_2$

$\text{H}_2\text{O}$ → $\text{HCl}$ → $\text{H}_2\text{S}$ → $\text{N}_2\text{O}$ → $\text{CH}_4$ → $\text{C}_2\text{H}_6$

$\text{Cl}$ → $\text{CH}_2\text{O}$

Fast chemical coupling

- Never detected
- Measured
- Airglow measured

Volcano, Hot spot

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Speculative chemistry

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Measured by MIRTIS

Airglow measured by MIRTIS

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Methane loss by electrochemistry

- - -

OH

CO

H₂O

NO₂

N₂

CO₂

HO₂

O₃

CH₄

OH

HO₂

CI

HCl

H₂S

N₂O

CH₄

C₂H₆

CH₂O
The case of Halogen species
Detection of perchlorate (ClO4-) by Phoenix MECA experiment is indicative of Cl species once outgassed into the atmosphere.
HCl, HF, HBr, etc....

None of these species have been detected to date.

Upper limits on HCl and H$_2$O$_2$

Herschel latest results give an upper limit of $\sim$200 ppt for HCl

< 200 ppt

< 2 ppb
The case of Sulfur species
Sulfur species on Mars

- **Sulfur species found at the surface**
  - Viking: sulfates in the soil (5-10%, Toulmin et al. 1977)
  - Spirit & Opportunity: sulfates minerals (>10%, Squyres et al. 2004)
  - OMEGA/MEx: Calcium sulfate (gypsum) identified at high N-latitudes (Langevin et al. 2005)

- However, no sulfur-bearing molecule has been found in the atmosphere
  - OCS < 70 ppb
  - H2S < 20 ppb
  - SO2 < 1 ppb thermal IR (Krasnopolsky 2005)
  - SO2 < 2 ppb submm (Nakagawa et al. 2009)
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SO2 upper limit – Krasnopolsky, Icarus 178, 48, 2005

Fig. 3. Sum of spectral intervals centered at the expected positions of sixteen SO2 lines and corrected for their continua (see text). Error bars show standard deviations of the summed points. Each subpixel is $d=0.00228$ cm$^{-1}$. $S=1.0 \times 10^{18}$ cm is the sum of the sixteen line strengths. The Gaussian has a width of the instrument spectral resolution (0.0177 cm$^{-1}$) and corresponds to the SO2 mixing ratio of 1 ppb in the martian atmosphere.

Model: SO2 = 1 ppb

SO2 < 1 ppb (2s) – Integration over Tharsis region
Ls = 205° (June 2003)
Search for SO$_2$ using high-resolution imaging spectroscopy in the thermal infrared

**Instrument:**
- **Spectral range:** 7.35 - 7.40 µm
- **Spectral resolving power:** 84000
- **Spatial resolution:** 1 arcsec
- **Date:** 12 October 2009
- **Ls:** 352° (equinox)
- **Mars diameter:** 6 arcsec

Encrenaz et al., 2011
2σ upper limit: SO2 < 0.3 ppb

TEXES data
Model SO2:
0.3 ppb, 0.5 ppb, 1 ppb, 2 ppb

Encrenaz et al., 2011
SO2 upper limit over the Martian disk

Long(Central Meridian) = 140 E

Line depth = 0.001 -> SO2 = 2 ppb

SO2 < 2 ppb everywhere on the disk
in particular at high N-latitudes

Region observed:
- Long: 50-170 E, lat > 30N
- Long: 100-170 E, 0 < lat < 30N
- Long: 110-170 E, 15S < lat < 0
Conclusions for sulfur species

- **SO2 upper limit (2σ):** 0.3 ppb at mid-northern latitudes, 2 ppb at all northern latitudes
- **SO2** is a non-condensible species with lifetime (2 yr) longer than global mixing (0.5 y)
  - homogeneous distribution is expected
- **No evidence for localized sources**
  - even around gypsum region
  - consistent with above statement (S-rich areas are not tracers of gaseous SO2)
- **No evidence for seepage at the Martian surface**
  - SO2/CH4 typically 10-4 – 10-3 in Earth volcanoes
  - If CH4 is present on Mars, seepage origin seems unlikely (cf. Krasnopolsky 2005)
The case of Methane
Detection of Methane in the Atmosphere of Mars

Valerie Finn, James Green, and James Parrot

Abstract

We report the detection of methane in the atmosphere of Mars. The observed global average mixing ratio of 10 ppbv amounts to a column abundance of $2 \times 10^{18}$ molecules cm$^{-2}$ CH$_4$ molecules at the surface of Mars. Assuming a CH$_4$ photochemical lifetime of $2 \times 10^6$ years, the CH$_4$ mixing ratio of 10 ppbv is consistent with a steady-state atmospheric concentration of CH$_4$.

Introduction

Methane is a strong greenhouse gas and a potential indicator of biological activity on Mars. Previous efforts to detect methane in the Martian atmosphere have been unsuccessful. In this study, we report the detection of methane with a global average mixing ratio of 10 ppbv, which is consistent with a steady-state atmospheric concentration of CH$_4$.

Experimental

We used the Pathfinder Flight System (PFS) to search for methane in the Martian atmosphere. The PFS is a hyperspectral imaging instrument that was carried onboard the Pathfinder spacecraft.

Results

The observed global average mixing ratio of 10 ppbv amounts to a column abundance of $2 \times 10^{18}$ molecules cm$^{-2}$ CH$_4$ molecules at the surface of Mars. Assuming a CH$_4$ photochemical lifetime of $2 \times 10^6$ years, the CH$_4$ mixing ratio of 10 ppbv is consistent with a steady-state atmospheric concentration of CH$_4$.

Discussion

The detection of methane on Mars has important implications for understanding the planet's climate and potential for habitability. Further studies are needed to determine the source of the methane and its implications for the Martian environment.

Figures

Fig. 1. (A) A portion of the first averaged PFS spectrum (January-February 2004, black curve), with three water lines (at 3003, 3022, and 3026 cm$^{-1}$) and two solar lines (at 3012 and 3014 cm$^{-1}$). The second water line is due to instrumental response function. (B) The second averaged PFS spectrum (May 2004) in the same frequency interval. The caption is the same as for (A). The SNR is about 1500.

Fig. 2. (A) Synthetic spectra computed for 0 ppbv (green curve) and 10, 20, 30, and 50 ppbv (violet curves) of methane, compared with the PFS average spectrum (black curve). The synthetic spectra have been computed for 0 ppbv of H$_2$O, along with dust and water ice clouds. The temperature profile obtained from simultaneous measurements in the thermal radiance was used. (B) Same as (A), with the PFS mean spectrum shown in Fig. 1B.
Fig. 1. (A) A portion of the first averaged PFS spectrum (January-February 2004, black curve), with ±1σ confidence (red lines). The SNR is about 1300. Methane is identified at 3018 cm⁻¹. There are three water lines (at 3003.5, 3022, and 3026 cm⁻¹) and two solar lines (at 3012 and 3014 cm⁻¹). The continuum slope is due to water ice clouds in the atmosphere. The small peak at the left of the main solar line is due to instrumental response function. (B) The second averaged PFS spectrum (May 2004) in the same frequency interval. The caption is the same as for (A). The SNR is about 1500.

Fig. 2. (A) Synthetic spectra computed for 0 ppbv (green curve) and 10, 20, 30, 40, and 50 ppbv (violet curves) of methane, compared with the PFS average spectrum (black curve). The synthetic spectra have been computed for 6.7 millibars of CO₂, including 350 ppm of H₂O, along with dust and water ice clouds. The temperature profile obtained from simultaneous measurements in the thermal radiation was used. (B) Same as (A), with the PFS mean spectrum shown in Fig. 1B.

Global Average: 10 ± 5 ppbv

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

- Two scenarios can explain the existence of CH4:
  - **Source Géophysique**: dégazage depuis les couches magmatiques ou par hydrothermalisme, apport exogène (comètes, météorites)
  - **Source Biologique**: décomposition d’une biomasse (gaz naturel), production métabolique, i.e. VIE

Methanogens in subsurface oceans would produce methane from their consumption of H, CO2, etc.

Serpentinization produces methane in undersea black smokers at Earth.
Two scenarios can explain the existence of CH4:

- **Geophysical source**: magmatic outgassing or hydrothermal sources

- **Source Biologique**: décomposition d’une biomasse (gaz naturel), production métabolique, i.e. VIE

\[
(\text{Fe,Mg})_2\text{SiO}_4 + n\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Fe}_3\text{O}_4 + \text{CH}_4
\]
The Martian methane puzzle

- Two scenarios can explain the existence of CH4:
  - **Source Géophysique**: dégazage depuis les couches magmatiques ou par hydrothermalisme, apport exogène (comètes, météorites)
  - **Biological source**: biomass decomposition (natural gas), metabolic production, i.e. Life

Methanogens in subsurface oceans would produce methane from their consumption of H, CO2, etc.

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]
However...

Mumma’s observations require:

- A Methane production rate (150,000 tons emitted) comparable to the entire Mid-Atlantic ocean ridge (Lefèvre and Forget, 2009)
- A Methane sink term 600x stronger than predicted by otherwise validated photochemical models (Lefèvre and Forget, 2009)
- Zahnle et al. (2011) provide lines of evidences that Martian CH4 lie in the vicinity of terrestrial 13CH4 lines
2011: Groundbased Observations

• Report by Mumma’s team at the Fourth International Mars atmosphere Workshop (Paris, February 2011):
  - 2009-2010 campaign
  - New instrument CRIRES: higher sensitivity and higher spectral resolution

• Results:
  - No methane detected (upper limit 1-5 ppbV)
2013: Mars Science Laboratory

SAM suite: search for organic molecules and study habitability
Atmospheric measurements:

CO2, CO, H2O, Ar, N2, CH4 (< 100 pptv)...

No detection of methane:
0 ± 1.1 ppbv

Webster et al. (Science, 2013)
2013: Mars Science Laboratory

SAM suite: search for organic molecules and study habitability
Atmospheric measurements:

CO2, CO, H2O, Ar, N2, CH4 (< 100 pptv)...

Future runs to come with 10x (at least) the current sensitivity (enrichment process)
Identifying the origin of Martian methane

Determining the origin of methane on Mars can only be addressed by looking at methane isotopologues and at higher alkanes (ethane, propane).

Genetic Zonation

ratio of methane/(ethane + propane) with $\delta^{13}$C (methane)

(available images and data)
“Something that is destroyed with a little extra precision is a myth.”

Paul Valéry, “Petite Lettre sur les mythes” 1930