

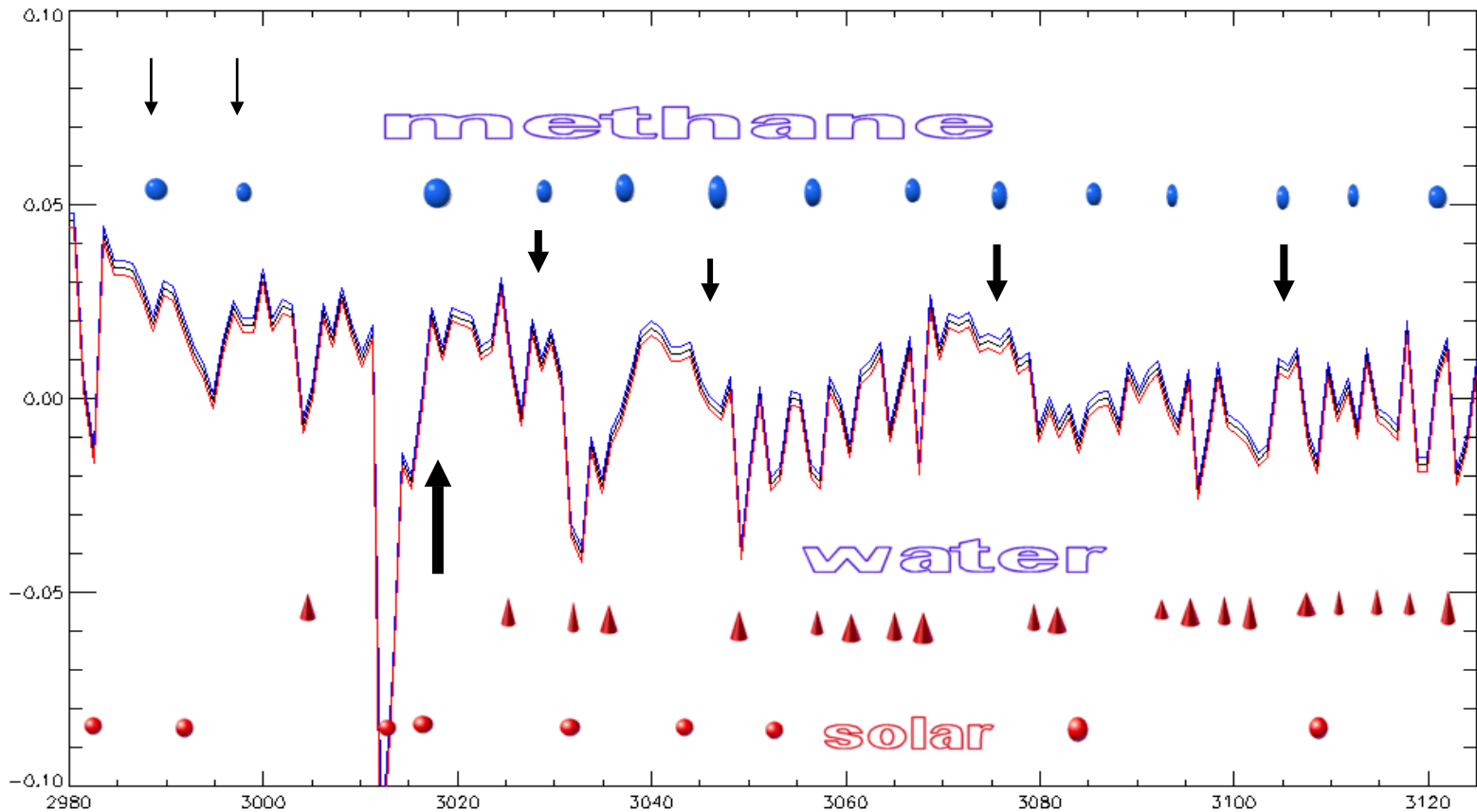
# THE SEARCH FOR LIFE ON MARS WITH PFS : METHANE , FORMALDEHYDE AND WATER .

By  
V. Formisano

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- 2 - FORMALDEHYDE (methane oxidised)
- 3 - WATER (the boundary layer and the neutron monitor)
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# METHANE (the surprising variations)

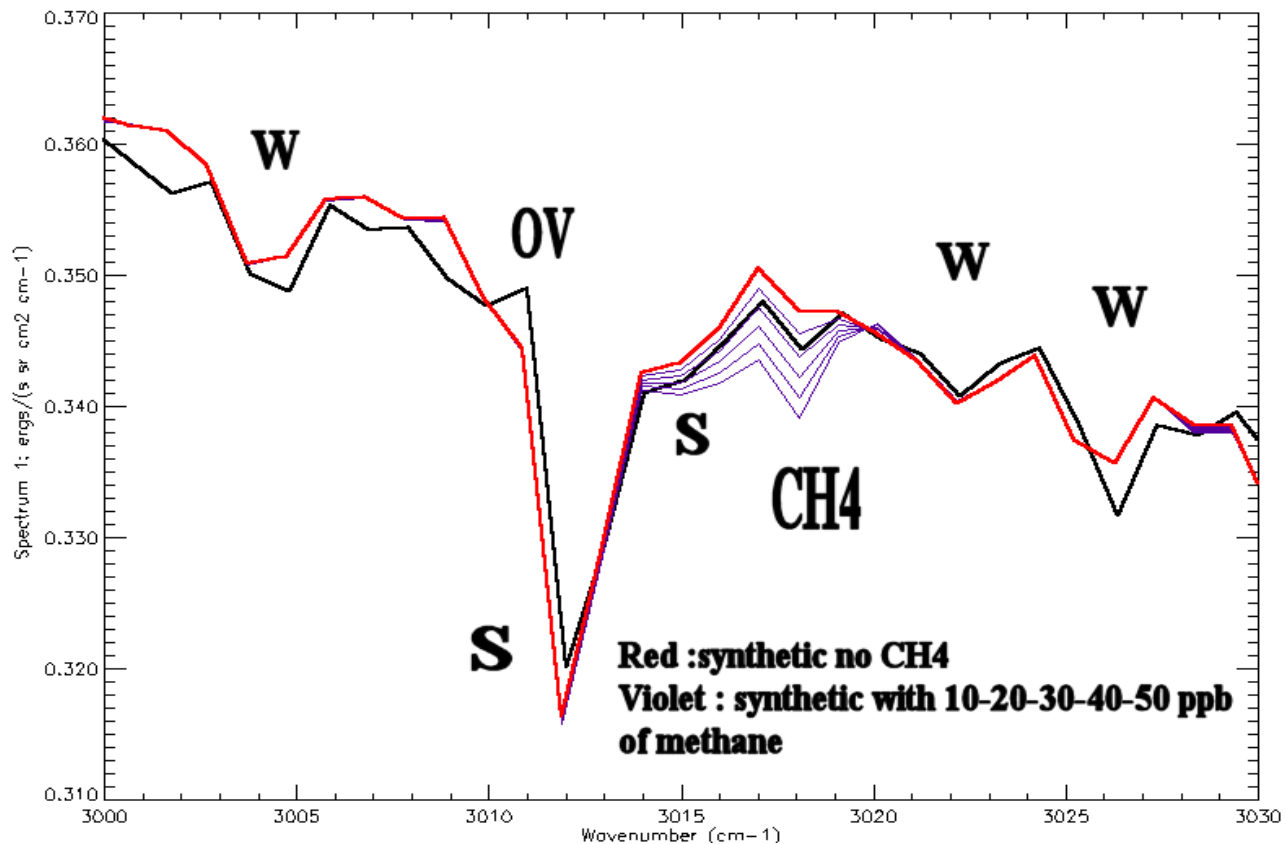


The first figure shown in March 2004 : a differential spectrum with indication of methane detection.

# Methane detection

Average over 1680 measurements.  $NER = 0.01/40 = 0.00025$  CGS

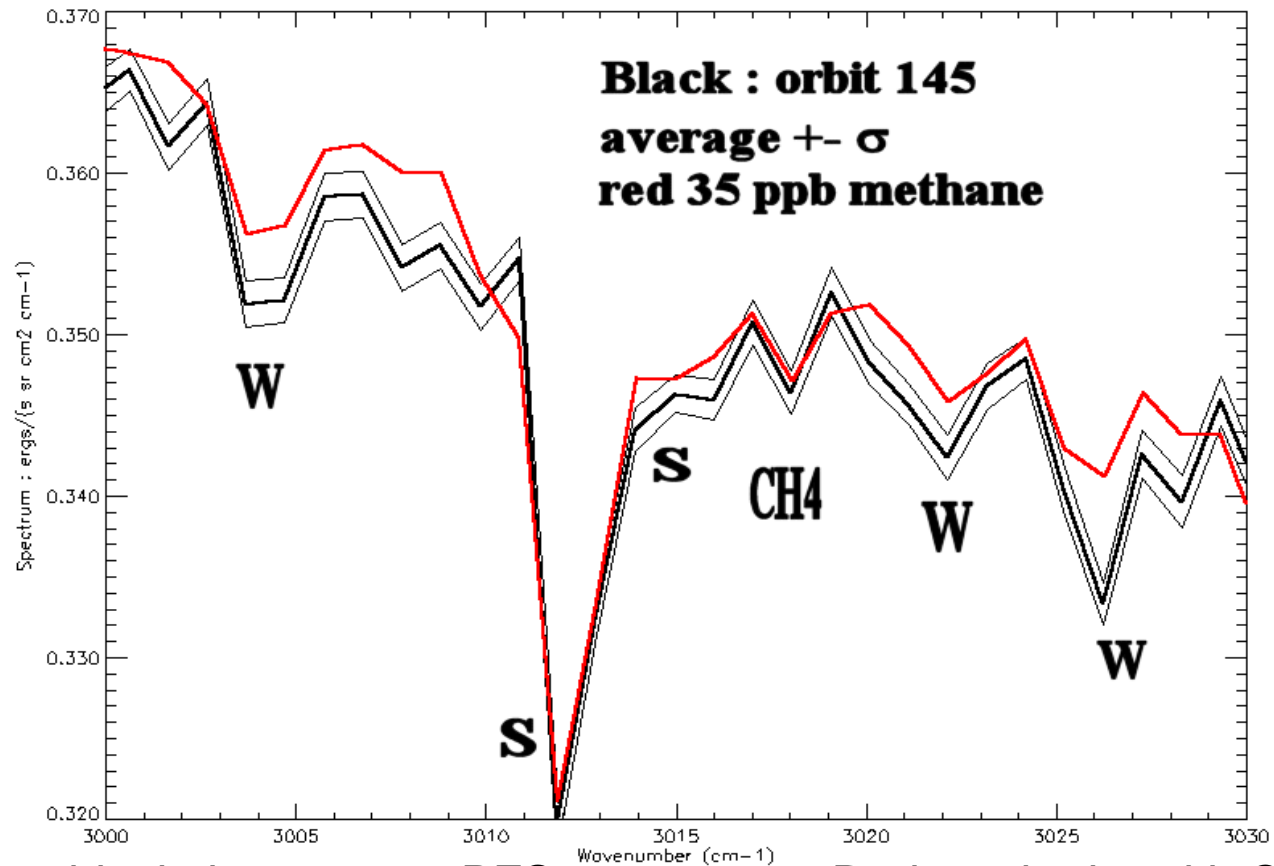
Detection is with  $> 10 \sigma$  confidence level.



Methane: black the average PFS spectrum ( 1680 m.) – Red synthetic , no CH4. Blue synthetic with CH4 ( 10-20-30-40-50 ppb) : 10+- 5 ppb.

# Methane variability

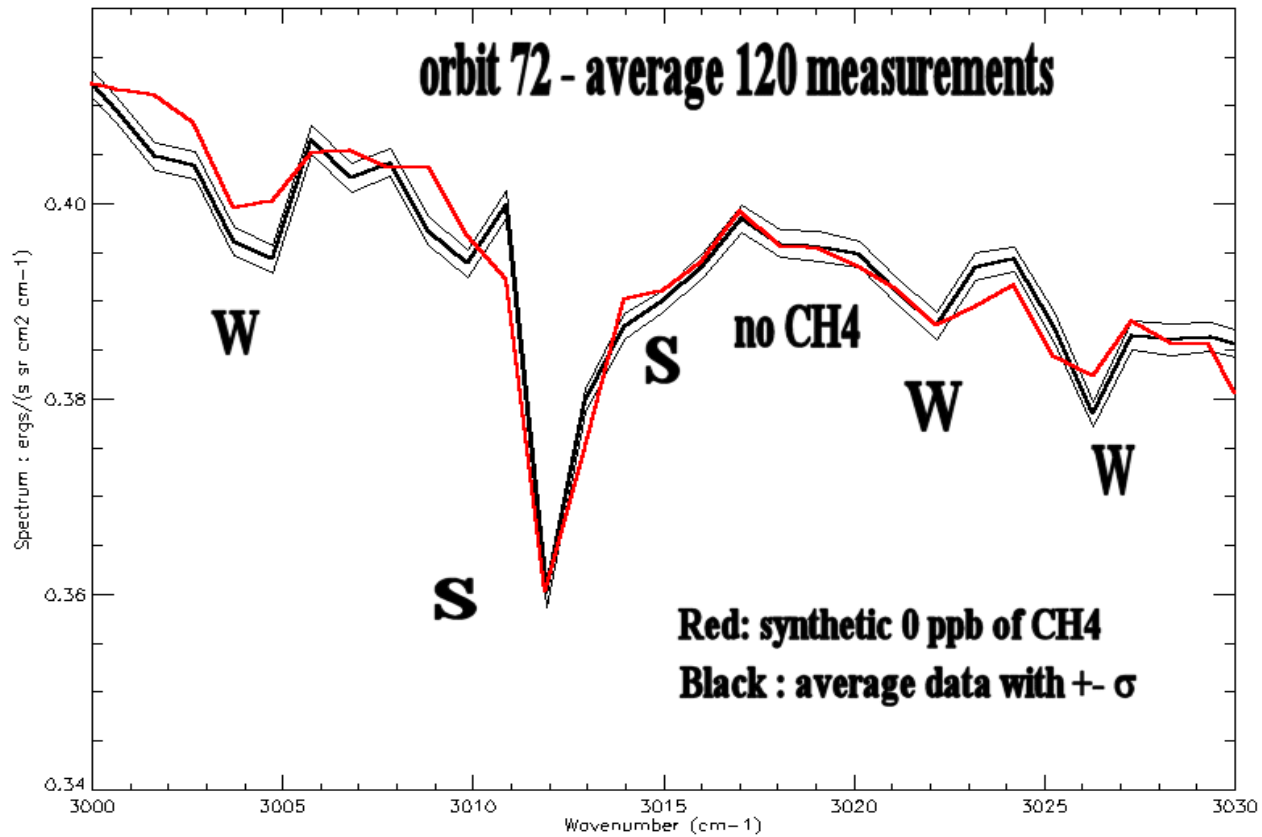
Average over 120 measurements.  $\pm 1$  sigma curves shown.



Methane: black the average PFS spectrum – Red synthetic with CH<sub>4</sub> (35 ppb).

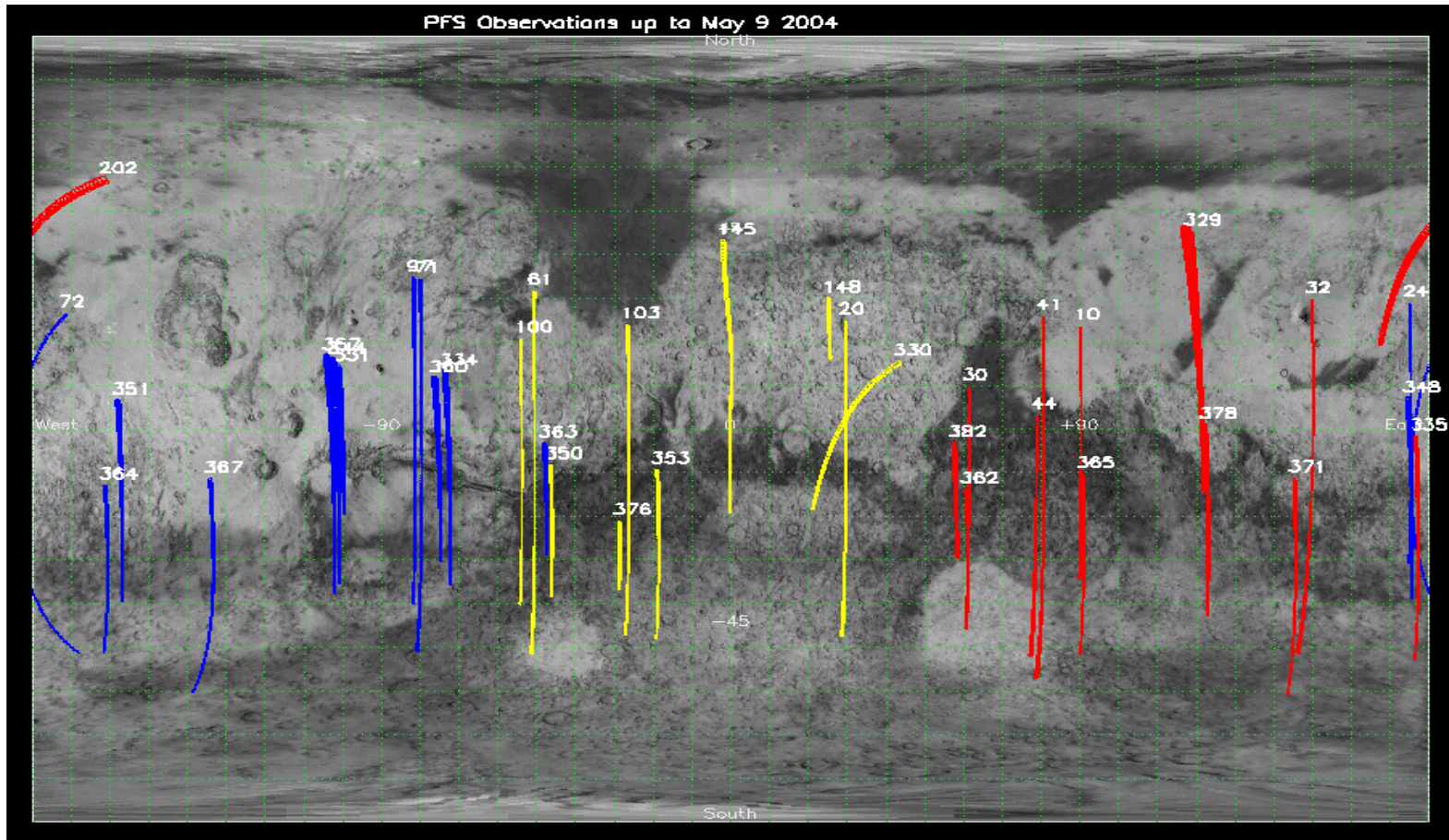
# Methane variability

Average over 120 measurements. + - 1 sigma curves shown.



Methane: black the average PFS spectrum – Red synthetic with CH<sub>4</sub> ( 0 ppb).

# Methane map



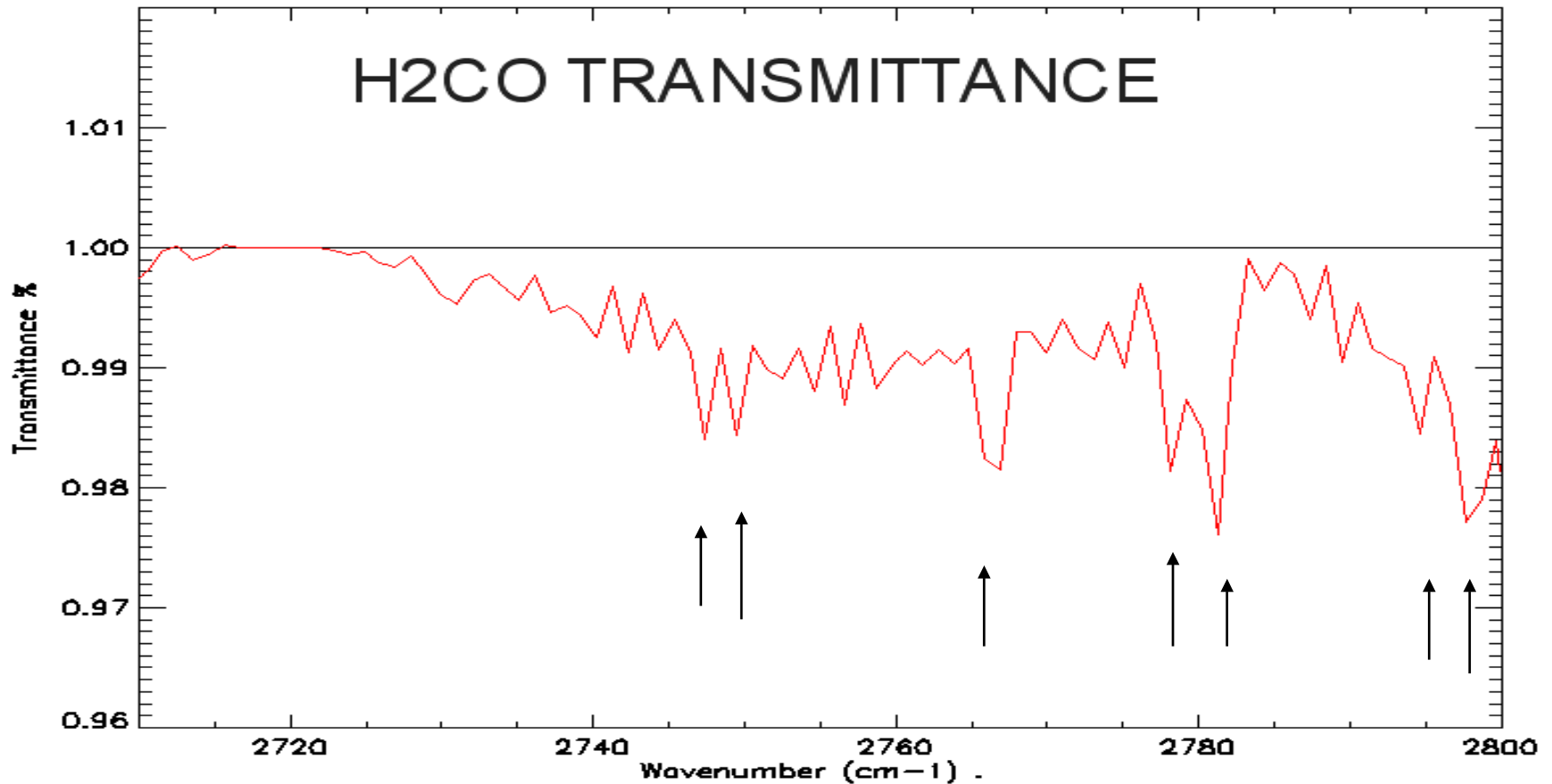
Red , yellow and blue : orbits with decreasing amount of methane. Orbital averages were used.

# Methane production

- The average 11 ppbv of methane in the martian atmosphere requires a production source of 150 ton/year
- The surprising feature is mixing ratio space variability.
- Possible sources are :
  - Hot chemistry 2 Km below the surface(up to 100 000 tons/year production rate).
  - Life under the surface
  - Exthernal source (comets?) or permafrost+radiation?



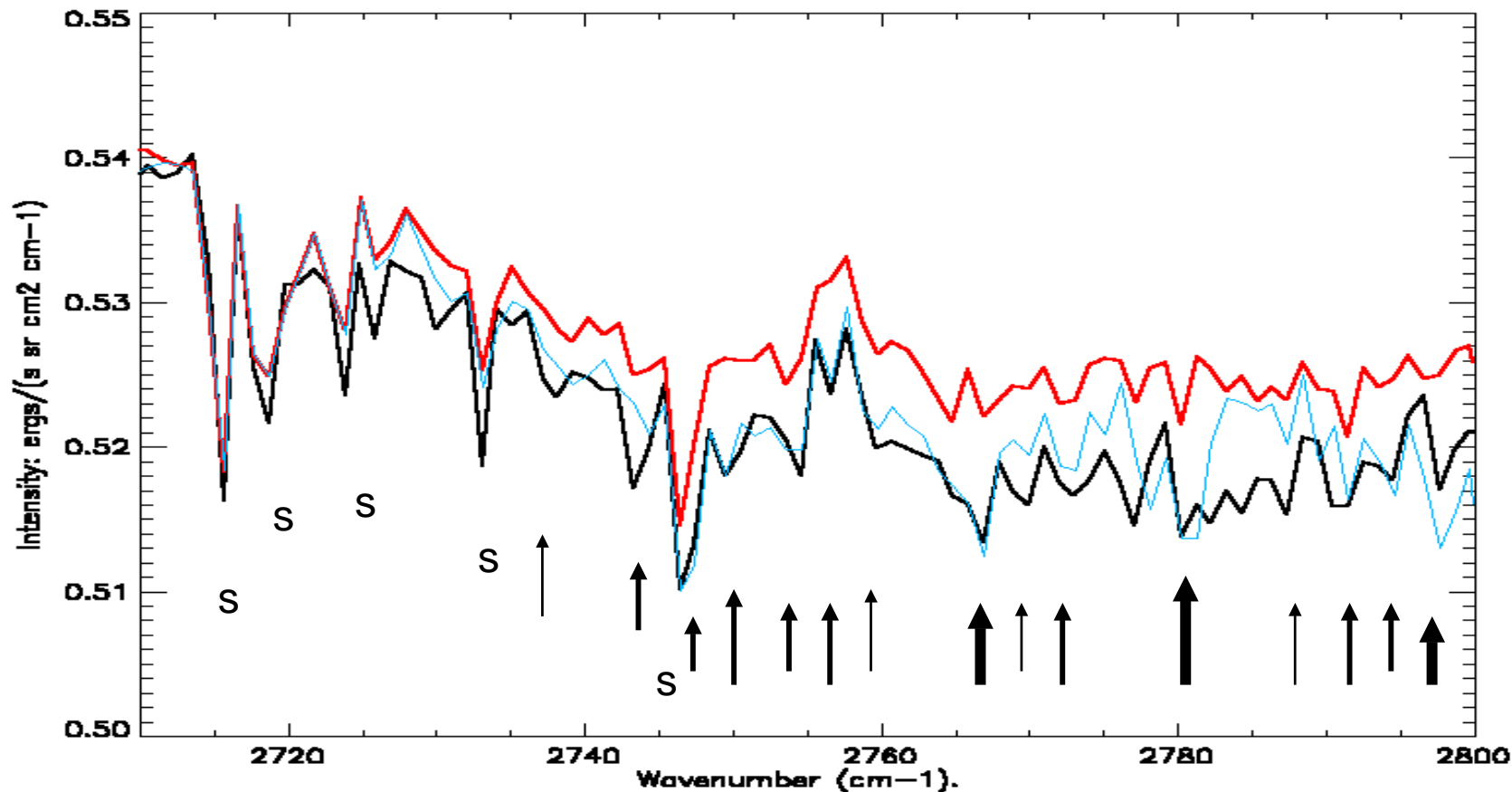
# Detection of formaldehyde



The red curve gives the % decrease of the radiance for 200 ppb of H<sub>2</sub>CO: it is 1% for the continuum and 1.5 – 2 % for the major lines.

# Detection of formaldehyde in orbit

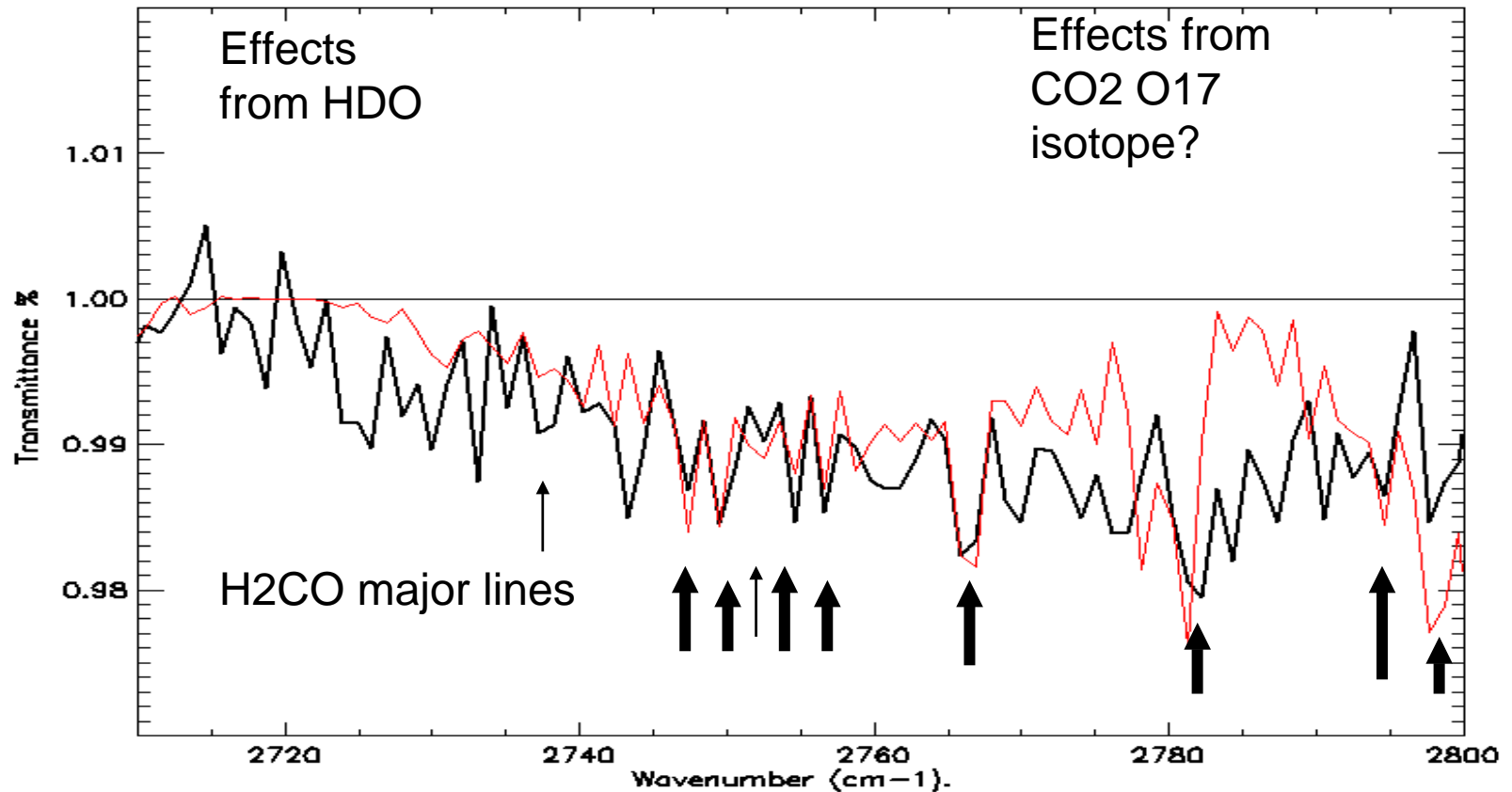
## 145 : 200 ppbv



Average over 120 measurements ( see the methane report ) . 15 possible lines identified. Note the good match in the 2710-2725 cm<sup>-1</sup> range.

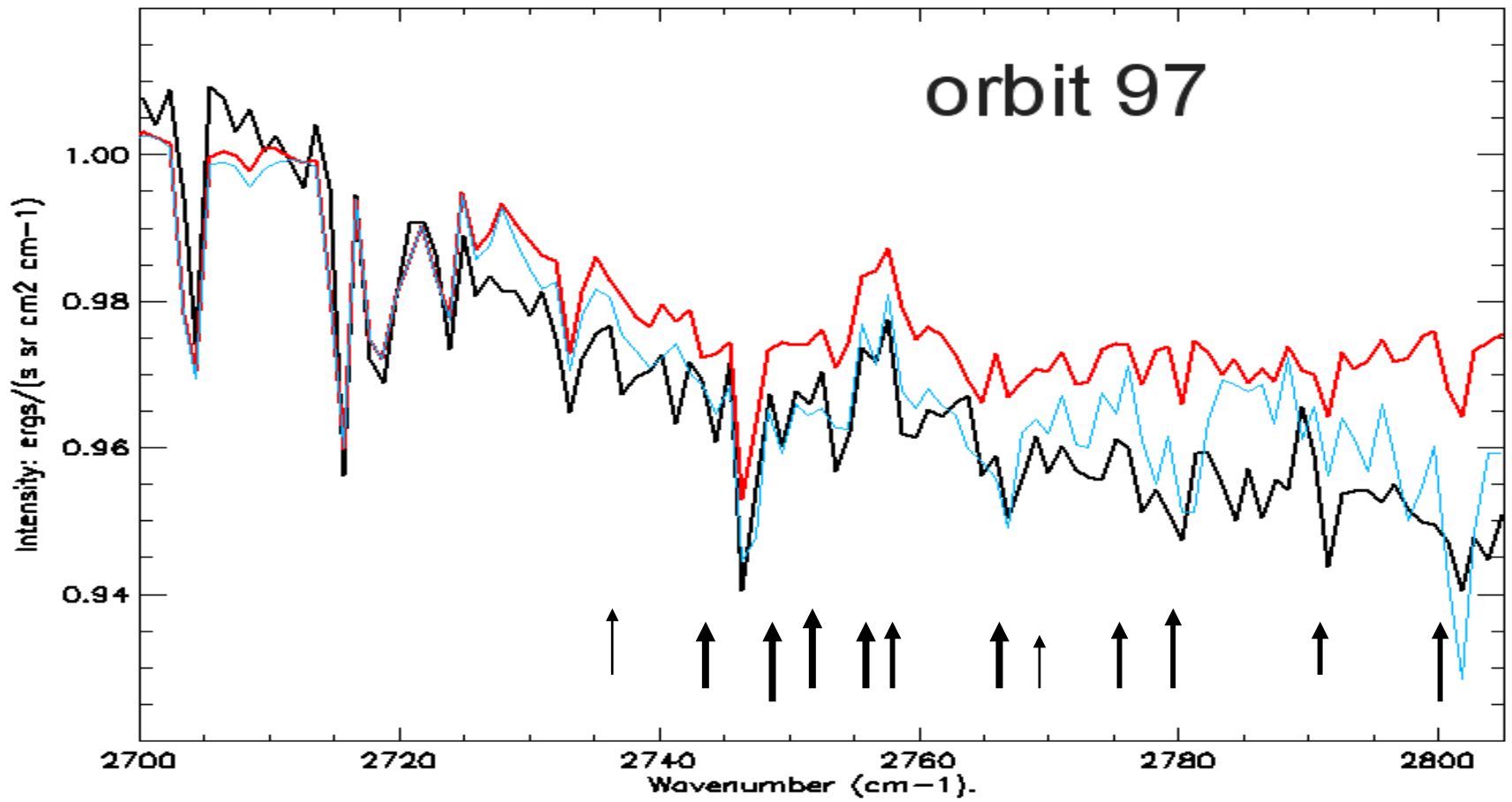
# Detection of formaldehyde for orbit 145 average

NOTE : 1% continuum decrease and 8 major lines of 1.5 – 2 % intensity



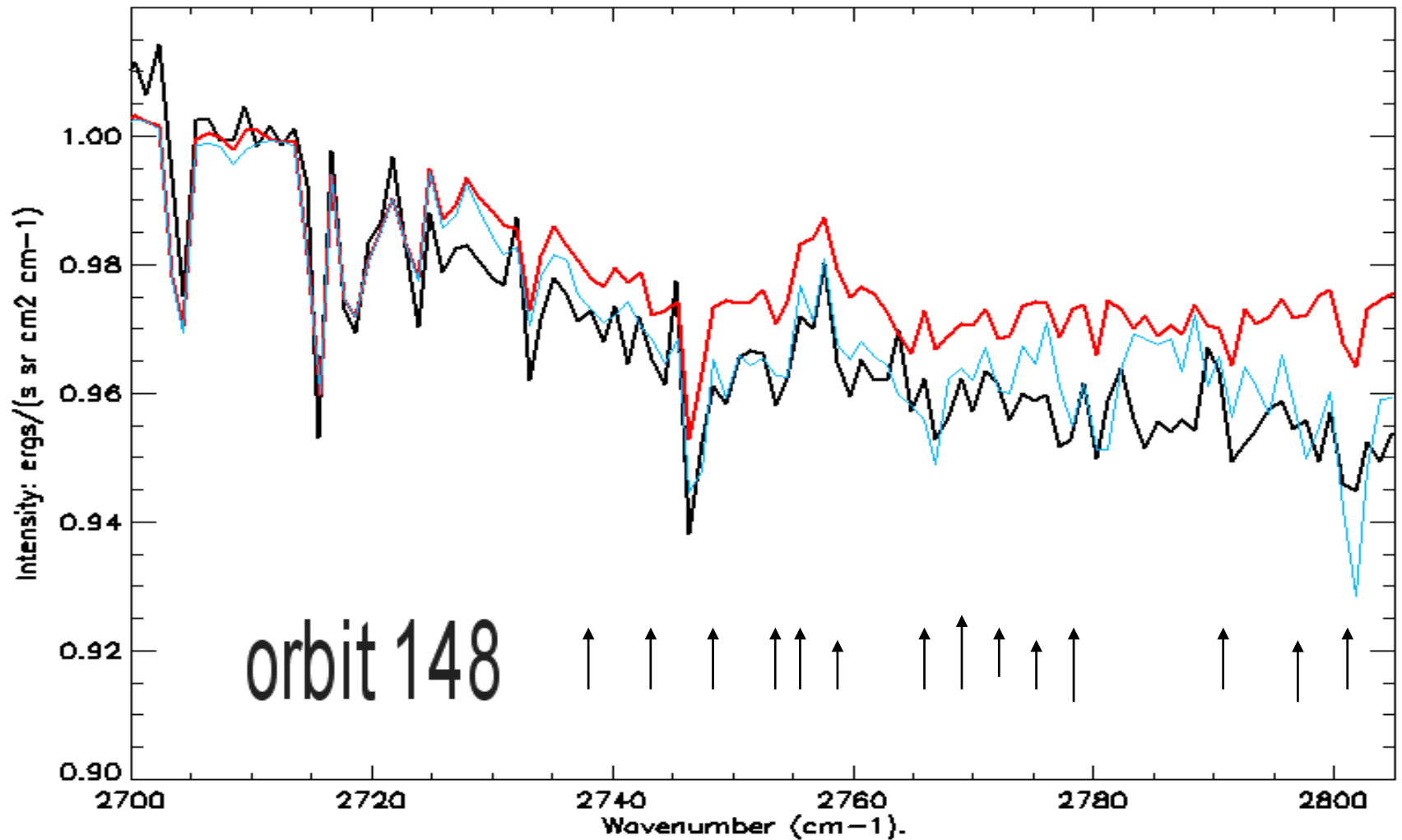
# Detection of formaldehyde in other orbits

( orbit 97 : averages over 140 measurements)



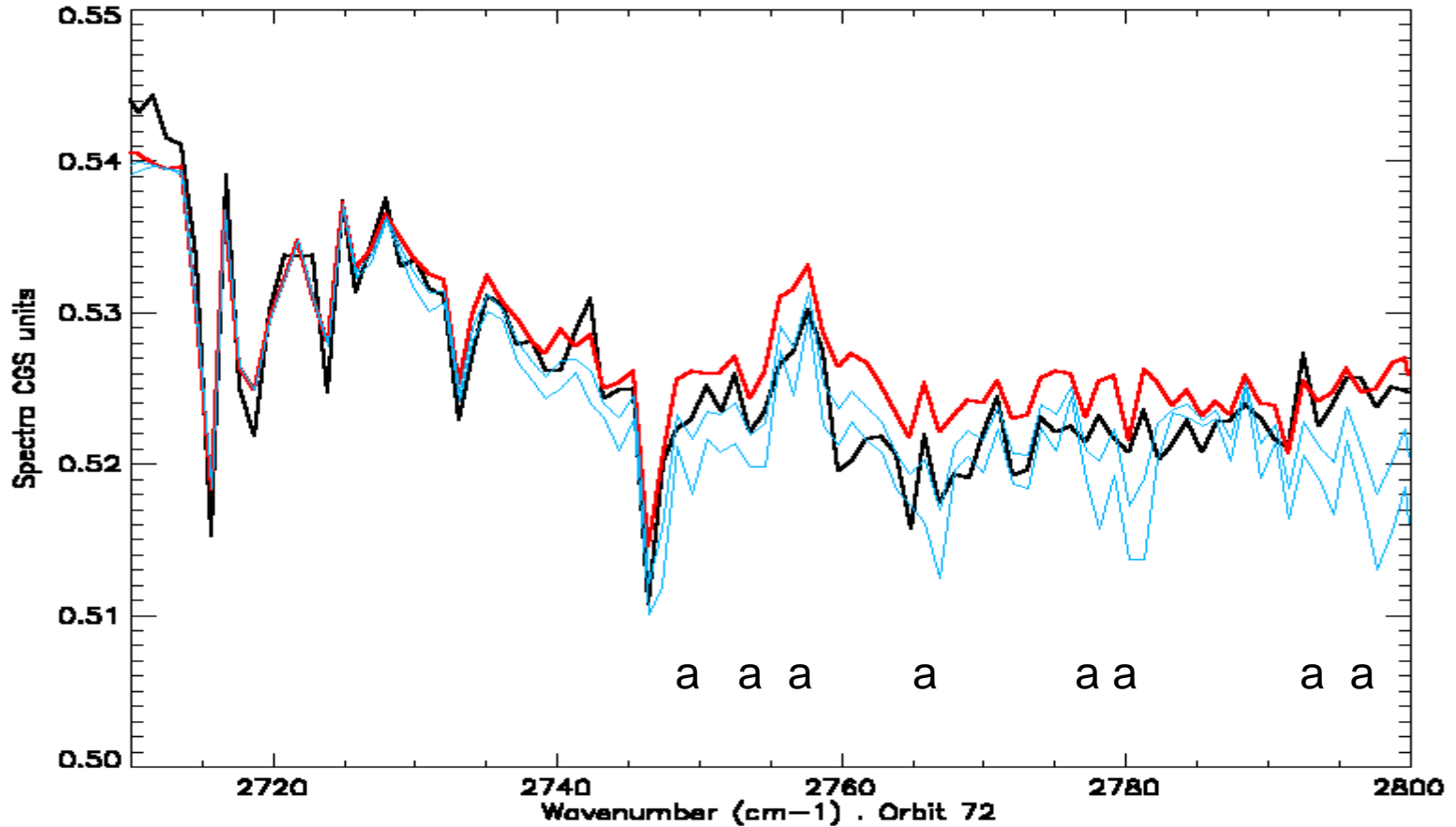
At least 12 lines identified.

# Detection of formaldehyde



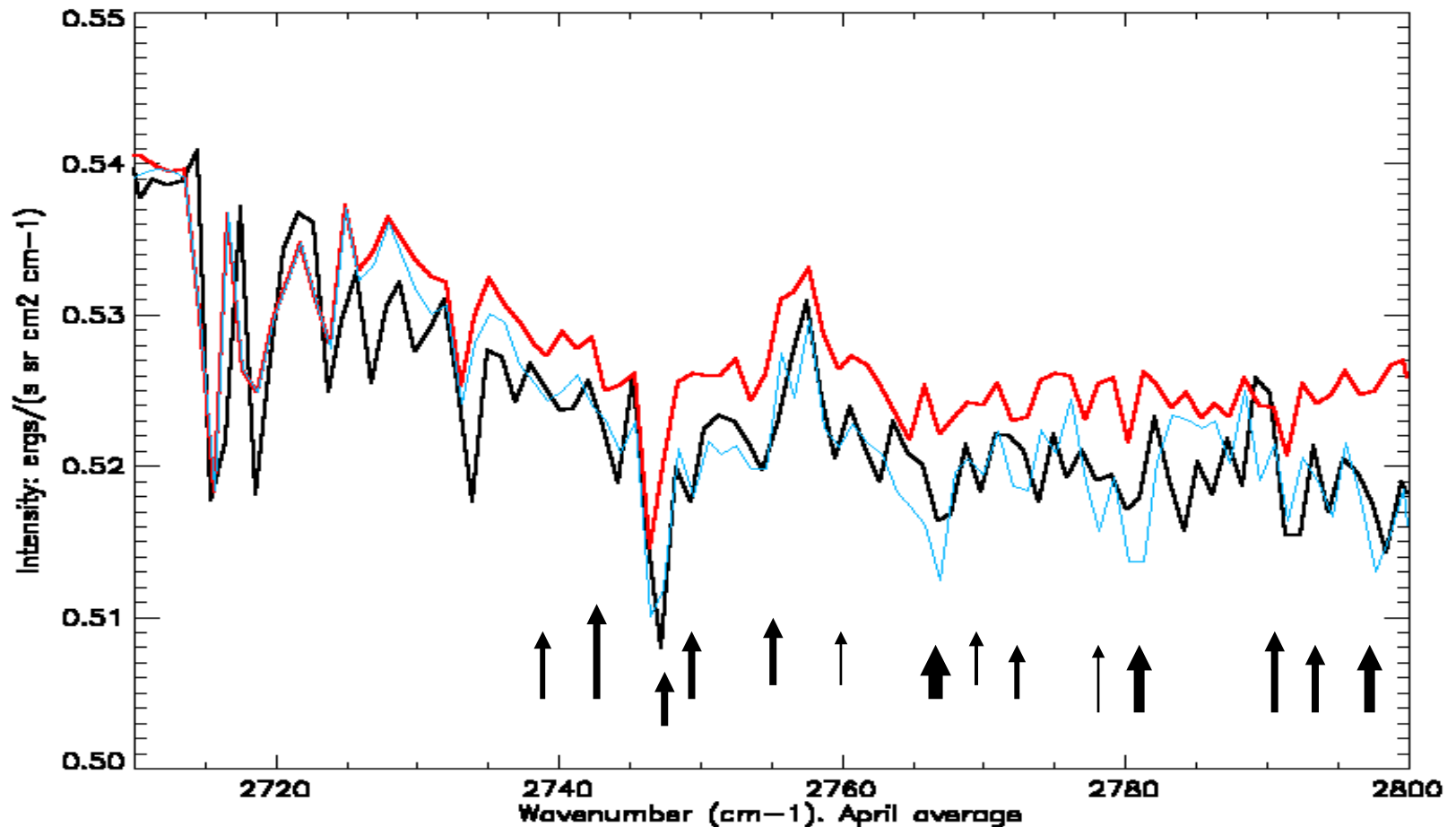
# Detection of formaldehyde :< 50 ppbv in orbit72

In this orbital average ( 120 meas.) 0 ppbv of methane was observed. The major CH<sub>2</sub>O lines are absent .



Note the good fit up to 2750 cm<sup>-1</sup> of the red curve.

Detection of formaldehyde: average value = 130 ppbv. 14 lines observed.



Black curve : average over 1680 measurements ( the same as for CH<sub>4</sub>).

# Detection of formaldehyde

- Formaldehyde has been detected correlated to methane.
- Formaldehyde variations are between <50 and 200 ppbv .
- The average mixing ratio is 130+-50 ppbv
- Further study is needed: in absence of oxidising conditions large quantities of methane could be observed ( see reports from Mumma).
- Methane must be 15-20 times more abundant if CH<sub>2</sub>O is oxidised methane



# Methane oxidation

ACCOUNTS  
of  
CHEMICAL  
RESEARCH®

DECEMBER 2003

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## Scientific Basis for Process and Catalyst Design in the Selective Oxidation of Methane to Formaldehyde

FRANCESCO ARENA\* AND  
ADOLFO PARMALIANA

*Dipartimento di Chimica Industriale e Ingegneria dei  
Materiali, Università degli Studi di Messina,  
Salita Sperone 31, I-98166 S. Agata (Messina), Italy*

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### ABSTRACT

The mechanism and kinetics of the gas-phase selective oxidation of methane to formaldehyde (MPO) are revised in the general

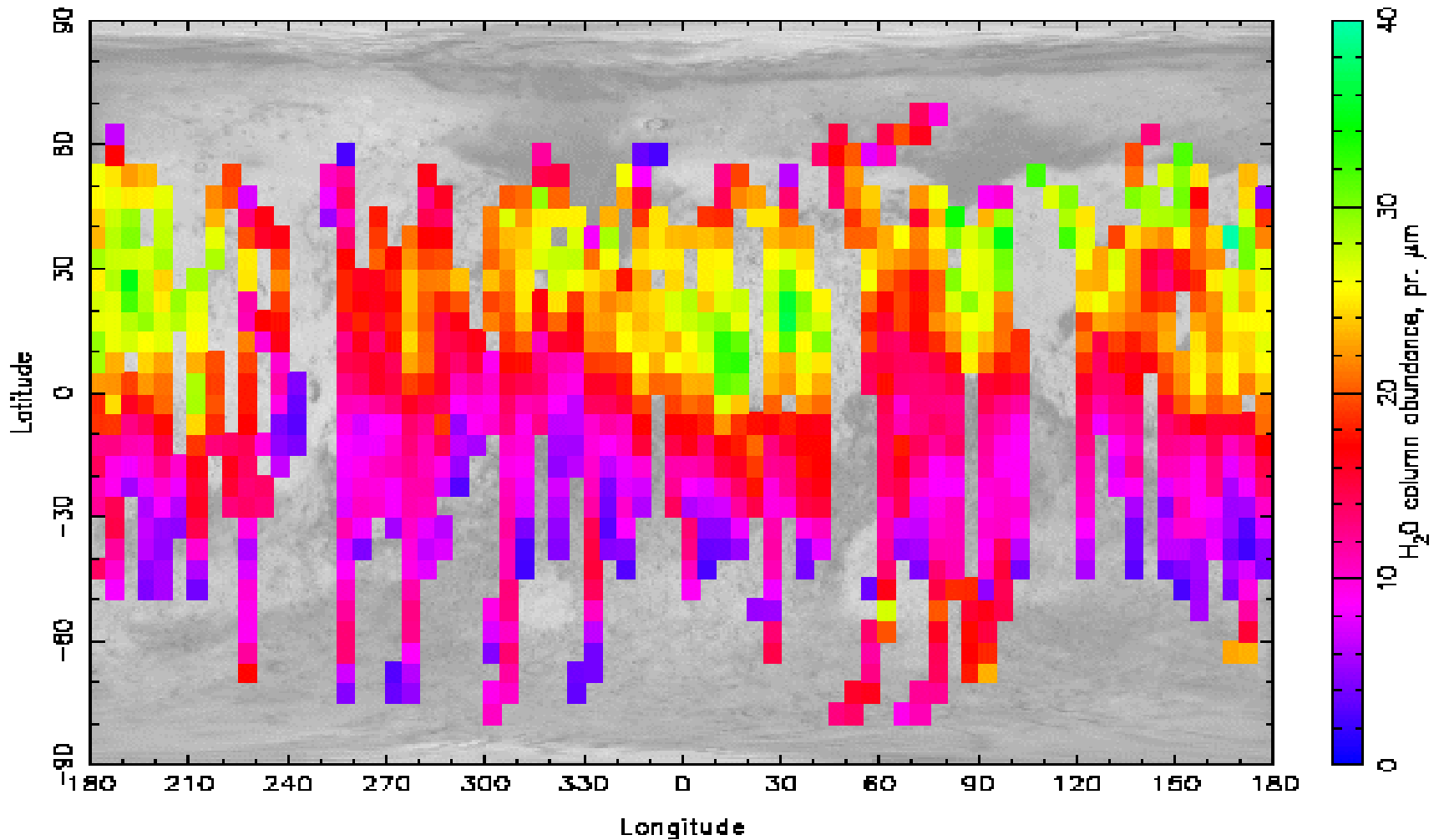
which in turn are used for making numerous finite products, from resins and plastics to paints, solvents, rubbers, drugs, etc. The economic impact of CSOs is considerable and amounted to a world turnover of ca. \$50 billion U.S. in 1998.<sup>1</sup>

Almost all CSO processes entail the specific functionalization of "reactive" organic substrates, such as alkenes and aromatics, which today are easily and cheaply obtained from crude oil, by selective oxidation, oxidative dehydrogenation, and oxidative ammonolysis reactions.<sup>1-4</sup> However, market forecasts indicate that, in the medium term, the petrochemical industry will move to a direct use of alkanes as feedstock rather than oil, these being even more economical, readily available, safer, and less toxic than olefins and aromatics.<sup>1-3</sup> This expected breakthrough in the petrochemical industry feedstock supply would be prompted by the worldwide abundance of natural gas (NG) reserves (consisting mainly of C<sub>1</sub>-C<sub>4</sub> alkanes) com-

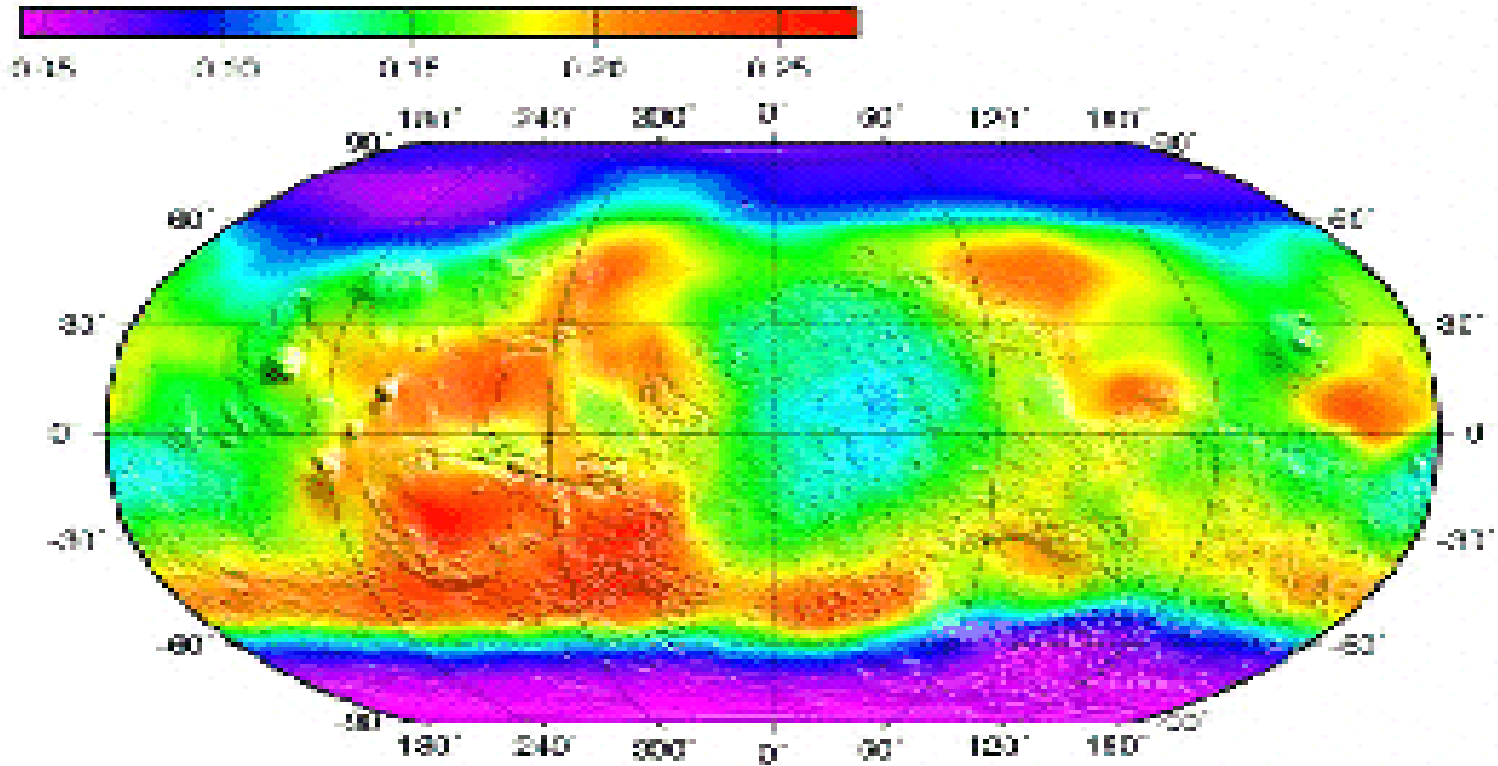
# Preferential oxidation

- Methane can be preferentially oxidised into formaldehyde in presence of iron oxides.
- In the Martian conditions, with the soil rich of iron oxides and in presence of adsorbed water and solar UV methane can possibly be **easily** oxidised into formaldehyde.
- (experiment done successfully in Germany , see results from Prof. Molmann)

# Water :boundary layer map

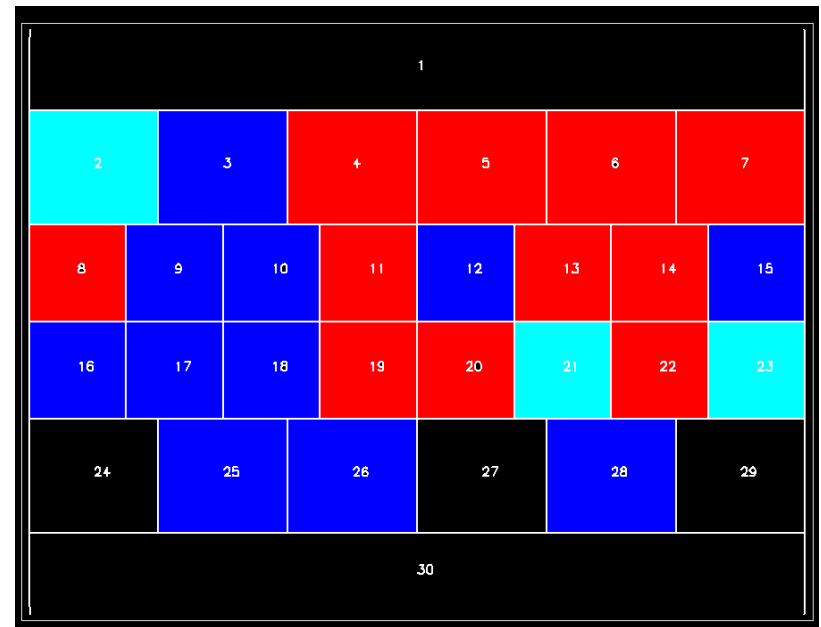
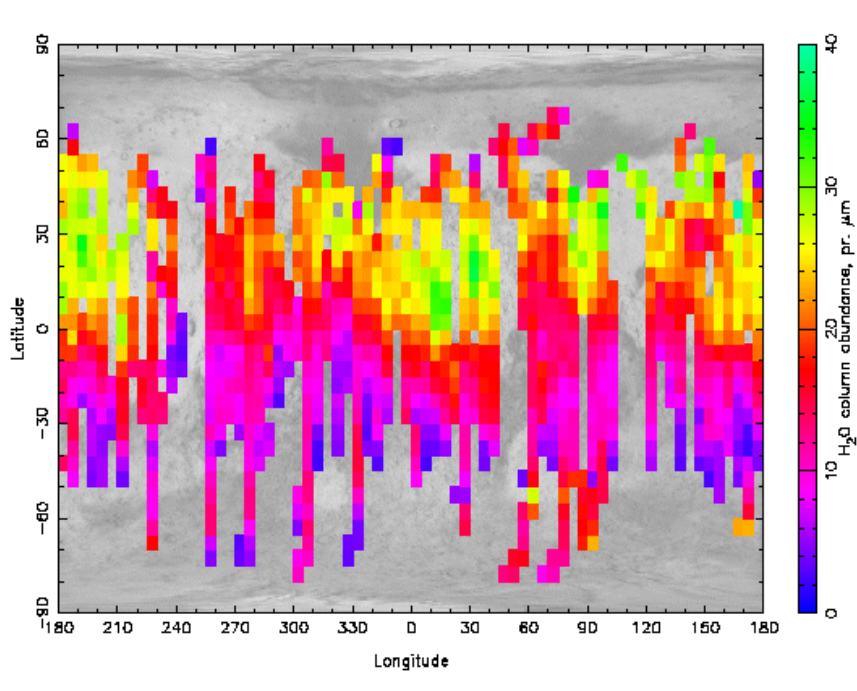


# Correlation with hend-Odissey



**Figure 1.** Map of epithermal neutron flux measured for frost-free martian surface.

# Correlation water-methane maps



IN THE 3 MAJOR REGIONS IN WHICH THE NEUTRON MONITOR FINDS AN ENRICHMENT OF WATER, WE SEE MORE BOUNDARY LAYER WATER AND MORE METHANE IN THE ATMOSPHERE.

# Pointing to the source

- A correlation exists in the atmosphere between water vapour in the boundary layer, methane and formaldehyde.
- The boundary layer water correlation with the Odissey HEND results points to an underground source producing water and methane.
- Methane is quickly oxidised (into formaldehyde ) when is injected into the atmosphere.
- Formaldehyde is destroyed in 7.5 hours in the atmosphere.

# On the possible sources of methane

- If methane alone is considered a source of 150 tons/year is needed.
- If  $\text{CH}_2\text{O}$  is considered as oxidised methane , a source of 2 500 000 tons/year is needed.
- On Earth methane production is 500 000 000 tons/year (200 times larger than Mars).

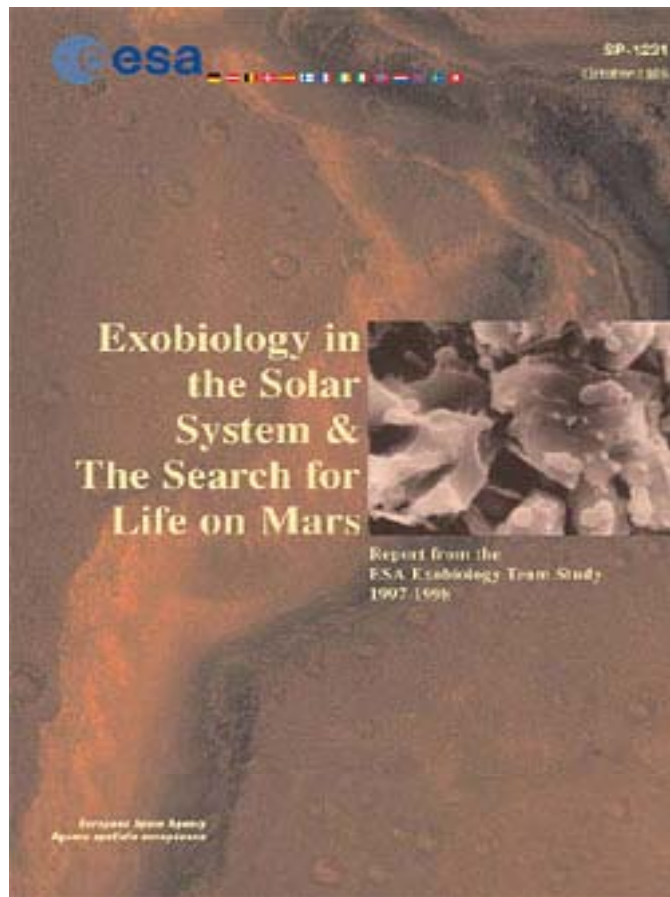
# On the possible sources of methane

- Underground hot chemistry can produce only 100 000 tons/year of methane (can this value increase?)
- Life in the vast areas of underground “water” seen by Odissey can produce methane
- Cosmic rays interaction with superficial permafrost can produce methane (modelling needed, not enough ?)



# 4 - IMPLICATIONS FOR LIFE ON MARS

- underground life can certainly provide enough methane to explain the observations of CH<sub>4</sub> and CH<sub>2</sub>O.
- It is not clear if the other possible sources are sufficient for the explanation of the observations.
- Methanogenic bacteria can be present 50 to 300 meters underground on Mars using H<sub>2</sub> , CO<sub>2</sub> to produce CH<sub>4</sub> : in presence of some sort of aquifer more complex biota could exist.
- I refer to the following book:




- I SHALL UNDERLINE A FEW STATEMENTS MADE IN THE ESA REPORT SP-1231 :
- EXO BIOLOGY IN THE SOLAR SYSTEM & THE SEARCH FOR LIFE ON MARS
- THESE STATEMENTS HAVE BEEN THE GUIDE TO MY RESEARCH :

# Where is life ?

These deep communities clearly suggest that life may also exist deep below the surfaces of other planets. Hence, we need to build this into any assessment of extraterrestrial life, as conditions for life may actually improve below the surface (e.g. Mars). The absence of surface life, therefore, may not necessarily indicate the absence of all life. Indeed, it seems rather naïve to limit the search for life to a planet's surface when we already know that the conditions are far beyond the possible ranges for life on Earth.

# Where is life ? Where is life ?

## I.3.6 Subterranean Life



For a long time, it was believed that deep subterranean environments were sterile. It has now been recognised that bacteria (and probably archaea, too) actually thrive in the terrestrial crust. Subterranean microorganisms are usually detected in subterranean oil-fields or in the course of drilling experiments (Parkes & Maxwell, 1993; Parkes et al., 1994; Stevens & McKinley, 1995). For example, recent research conducted within the International Ocean Drilling Program (ODP) has demonstrated that procaryotes are present much deeper in marine sediments than was previously thought possible, extending to at least 750 m below the sea floor, and probably much deeper (Parkes et al., 1994). These microbial populations are substantial (e.g 10<sup>7</sup> cells cm<sup>-3</sup> at 500 m below sea floor) and likely to be widespread. To depths of at least 432 m, microbes have been identified as altering volcanic glass, which comprises a substantial volume of the volcanic component of the ocean crust (Furnes et al., 1996), and may have significance for chemical exchange between the oceanic crust and ocean water. These data provide a preliminary, and probably conservative, estimate of the biomass in this important new ecosystem: about 10% of the surface biosphere. These discoveries have radically changed our perception of marine sediments and indicate the presence of a largely unexplored deep bacterial biosphere that may even rival the Earth's surface biosphere in size and diversity!

## In other words

hints for Life existing on Mars today are becoming stronger: PFS results cannot prove it , but is the best can be done from remote sensing.