
Unusual CO behaviour.
A relation to methane?
by
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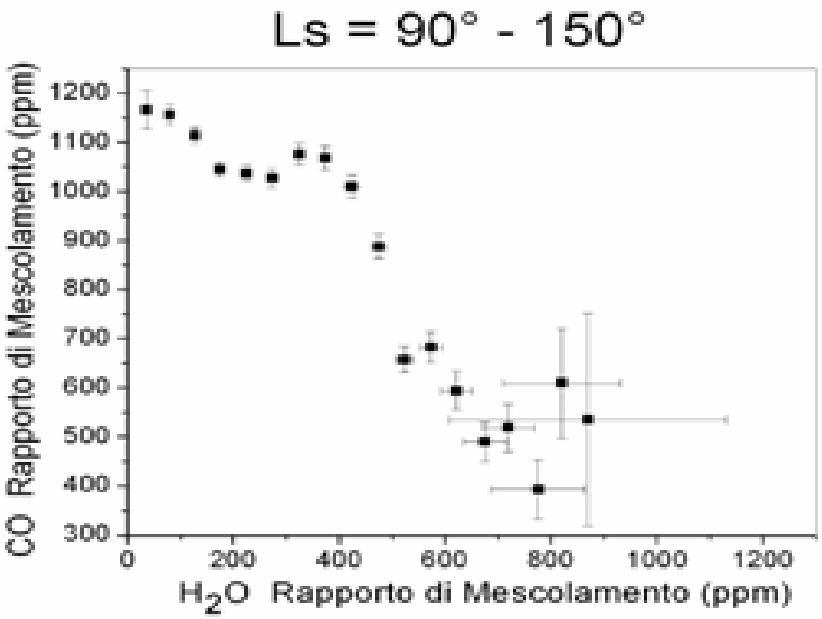
Normal CO behaviour

- CO is , in Martian atmosphere, produced by UV dissociation of CO2.
- H2O photochemistry produces a cathalizer that bring part of CO back to CO2.
- H2O and CO are therefore anticorrelated, mostly because of the CO2 condensation at one pole(winter), while water sublimate at the other pole(summer) .
- H2O enhancement should not go with CO enhancement.

Global circulation and CO

H2O- CO anticorrelation study

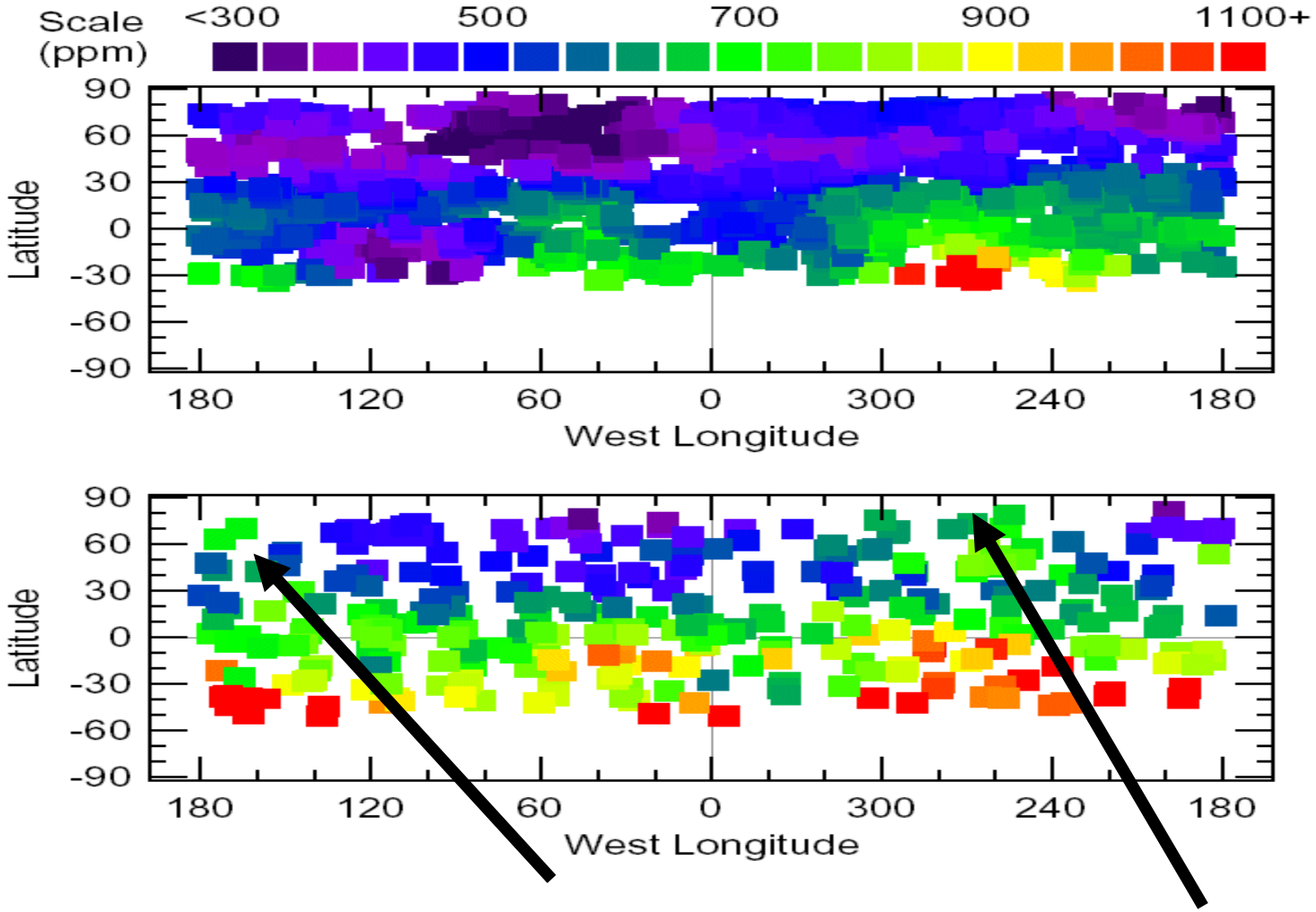


- Only during the northern summer we have found a good anticorrelation between the water vapor and the CO mixing ratio, due to northern polar cap sublimation with the southern polar cap CO2 condensation.

A strange behaviour

- There are cases , in northern summer, in which the anticorrelation shown previously is not valid, and a correlation is observed.
- We quote first observations from M.Smidth who studied the Crism data in spring and summer :

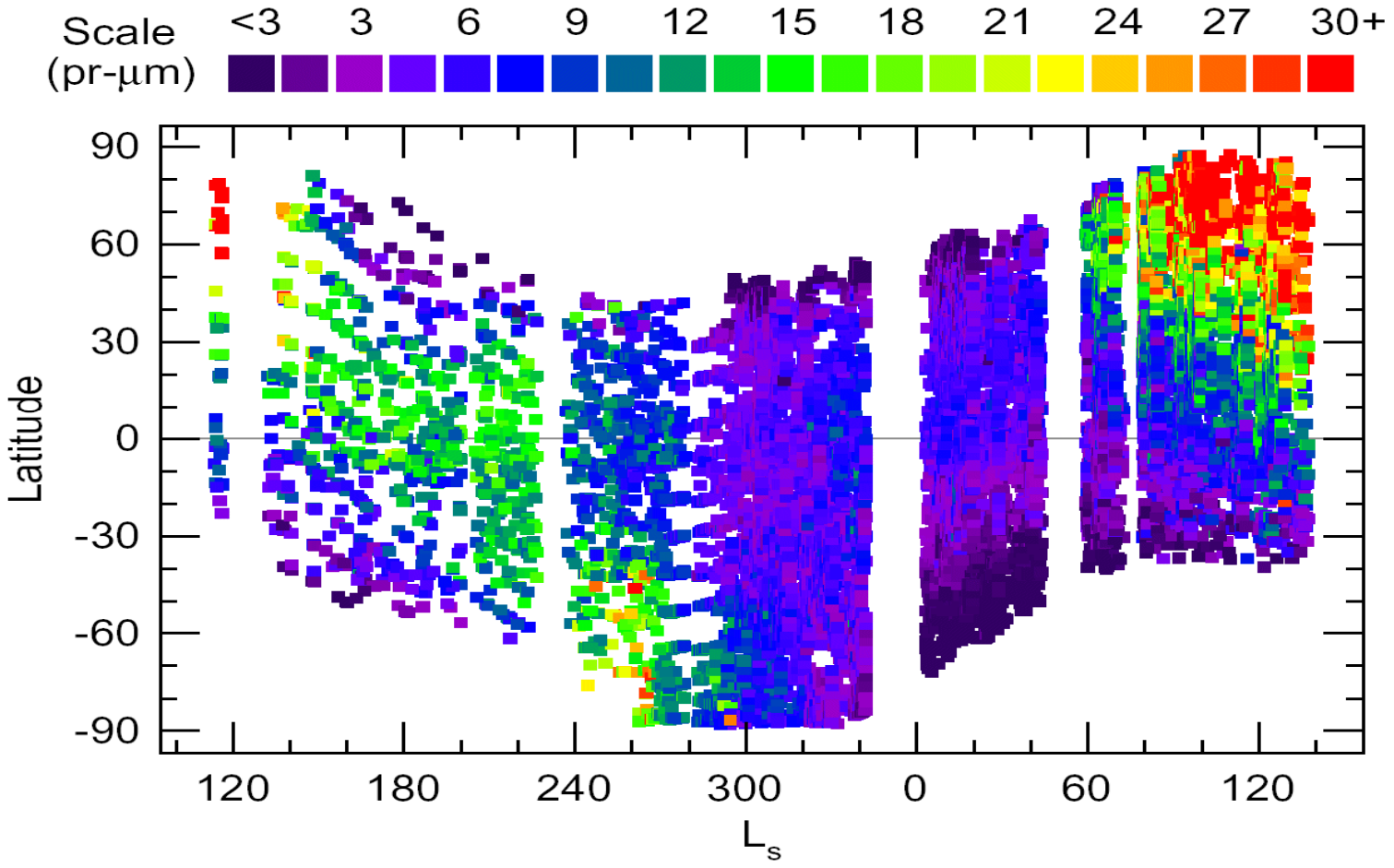
Global circulation and CO



Smidth et al . 2009 : top Ls= 75-105. Bottom Ls= 135-165.

High CO

Water vapor behaviour

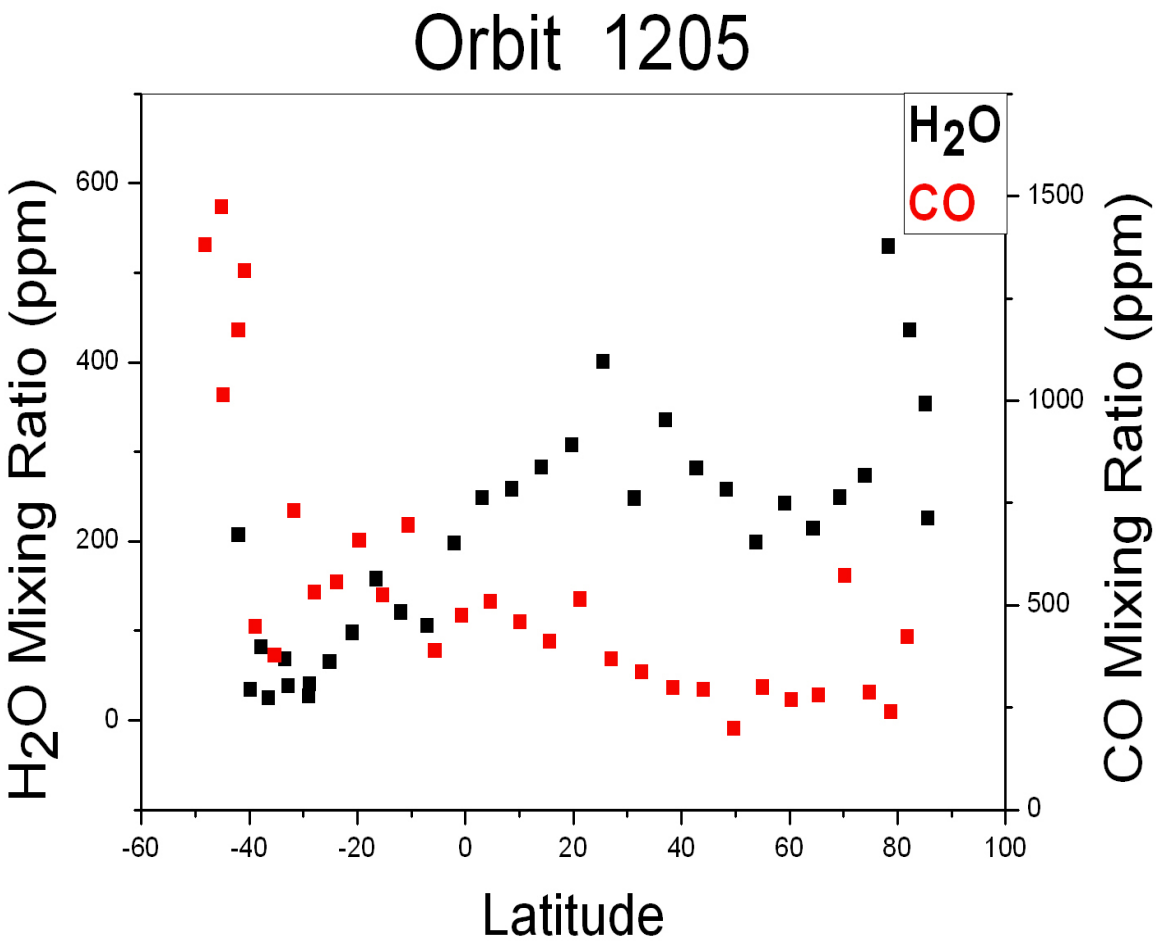


Smidth et al . 2009

Global circulation and CO

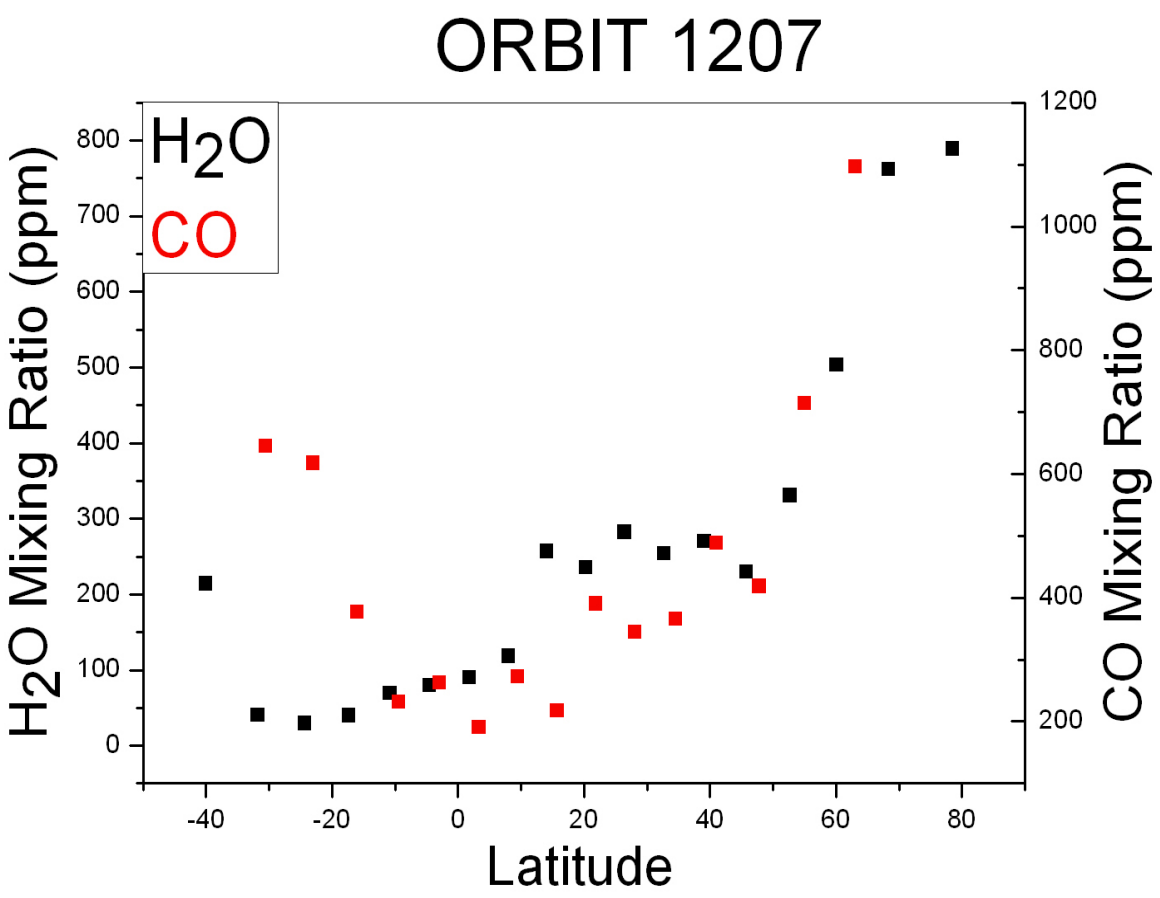
- In northern summer, toghether with a large increase of H2O vapor/ aerosols, there is also, occasionally, an increase of CO.
- The longitudes of this CO enhancements are : 150 – 180 and 200- 300 west longitudes, but probably may also change.
- PFS has also observed this anomalous behaviour:

PFS normal observations



In this orbit, which is in northern summer we observe the usual anticorrelation : CO in the southern hemisphere is enriched, while water vapor is enriched in the northern hemisphere.

PFS observation of CO anomaly

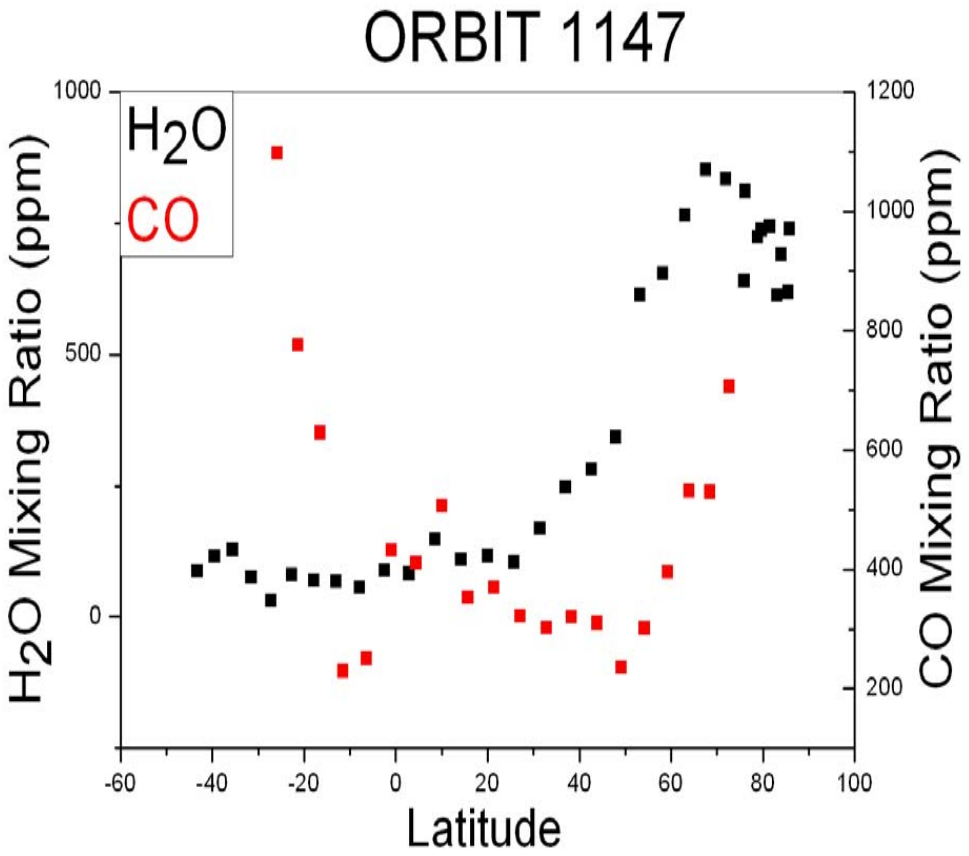


Ls= 135

E Long.= 155°

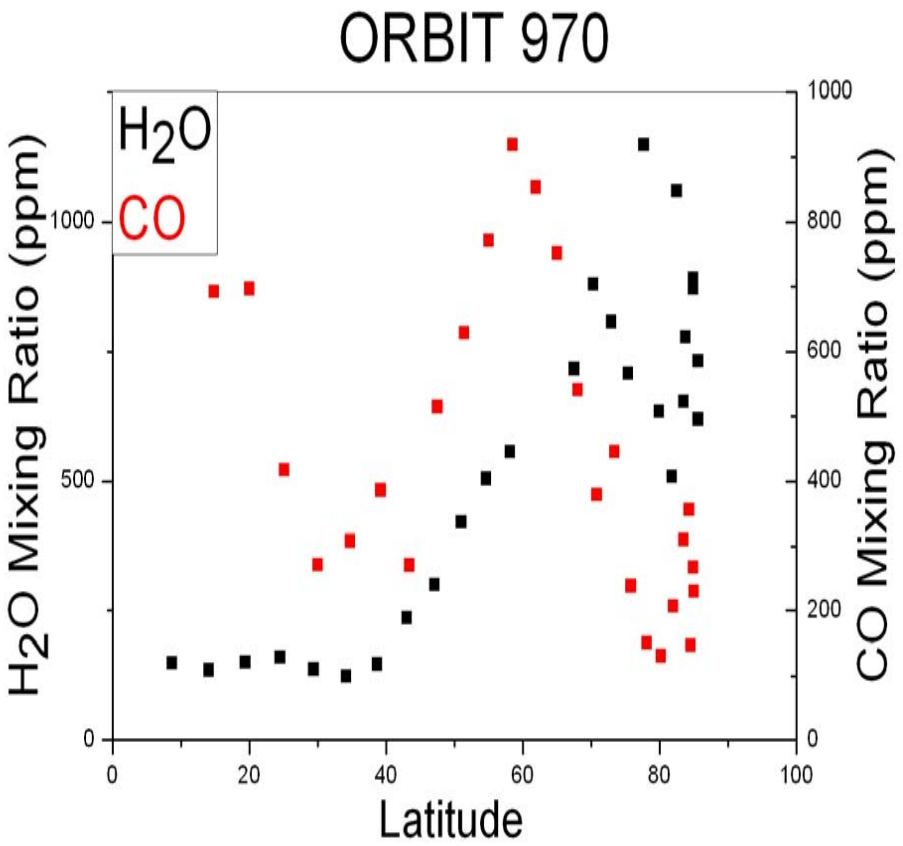
Here CO and water vapor increase toghether toward the north pole

PFS observation of CO anomaly



- Ls=126
- E Long=-72
- This is another example of the anomalous behaviour of CO; with lower intensity

PFS observation of CO anomaly



- Ls= 103
- E Long = 16
- This is another example of the anomalous behaviour of CO; up to 60 deg north latitude at least.

conclusions

- In the north hemisphere during the hottest summer period, PFS and CRISM observe at certain longitudes a strong enhancement of CO, simultaneously with an enhancement of the water vapor mixing ratio.
- It is not clear if this enhancement could be explained simply with the global circulation: from the GCM modelling (see next slide) it seems the enhancement cannot be due to the general circulation.
- If the global circulation cannot produce the observed CO enhancement, a possible explanation is a local source of CO, which must be contained in the surface polar ice because in spring is not observed. Possibly the clathrate hydrate that bring methane into the atmosphere have also CO?

Global circulation modelling

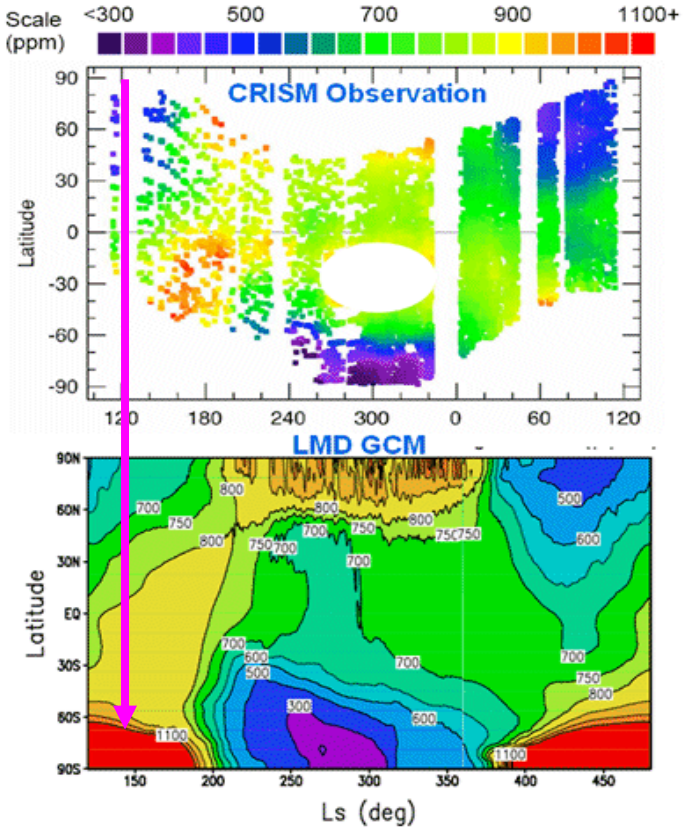


Figure 2: The mixing ratio of carbon monoxide as a function of season (Ls) and latitude as observed by CRISM during Mars Years 28 and 29 [4] compared to the GCM prediction. The local maximum observed near Ls=300 is hidden to facilitate the comparison since it is an artifact due to a planet-encircling dust storm [4]

- From the F.Forget et al. 2009 paper: up, CRISM CO observations, down GCM modelling. The vertical line shows the Ls when the unusual observations were made. In the northern hemisphere there is no CO increase predicted when the water vapour has a maximum.

Assuming CO in the polar ice: Life is able to use CO

et al., 1994). The chemical reactions involved are:

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$$ Eq.1

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

Microbial colonies could exist in the subpermafrost aquifer environment of Mars, where microorganisms utilize CO and/or H_2, and produce methane in turn. The Martian atmosphere provides a ready source of CO (~700 ppmv) and H_2 (40–50 ppmv), based on models and observations (Atreya and Gu, 1994, 1995; Nair et al., 1994; Krasnopolsky, 1993). These gases are expected to diffuse

Here we quote Atreya et al PSS 2007, when discussing possibility of life as source of methane.

Life and CO

MOLECULAR BIOLOGY AND EVOLUTION

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Research Article

The Stepwise Evolution of Early Life Driven by Energy Conservation

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Abstract

Two main theories have emerged for the origin and early evolution of life based on heterotrophic versus chemoautotrophic metabolisms. With the exception of a role for CO, the theories have little common ground. Here we propose an alternative theory for the early evolution of the cell which combines principal features of the widely disparate theories. The theory is based on the extant pathway for conversion of CO to methane and acetate, largely deduced from the genomic analysis of the archaeon *Methanosarcina acetivorans*. In contrast to current paradigms, we propose that an energy-conservation pathway was the major force which powered and directed the early evolution of the cell. We envision the proposed primitive energy-conservation pathway to have developed sometime after a period of chemical evolution but prior to the establishment of diverse protein-based anaerobic metabolisms. We further propose that energy conservation played the predominant role in the later evolution of anaerobic metabolisms which explains the origin and evolution of extant methanogenic pathways.

Key Words: Methanosarcina acetivorans • energy conservation • methanogenesis • acetate kinase • phosphotransacetylase

Lab experiments

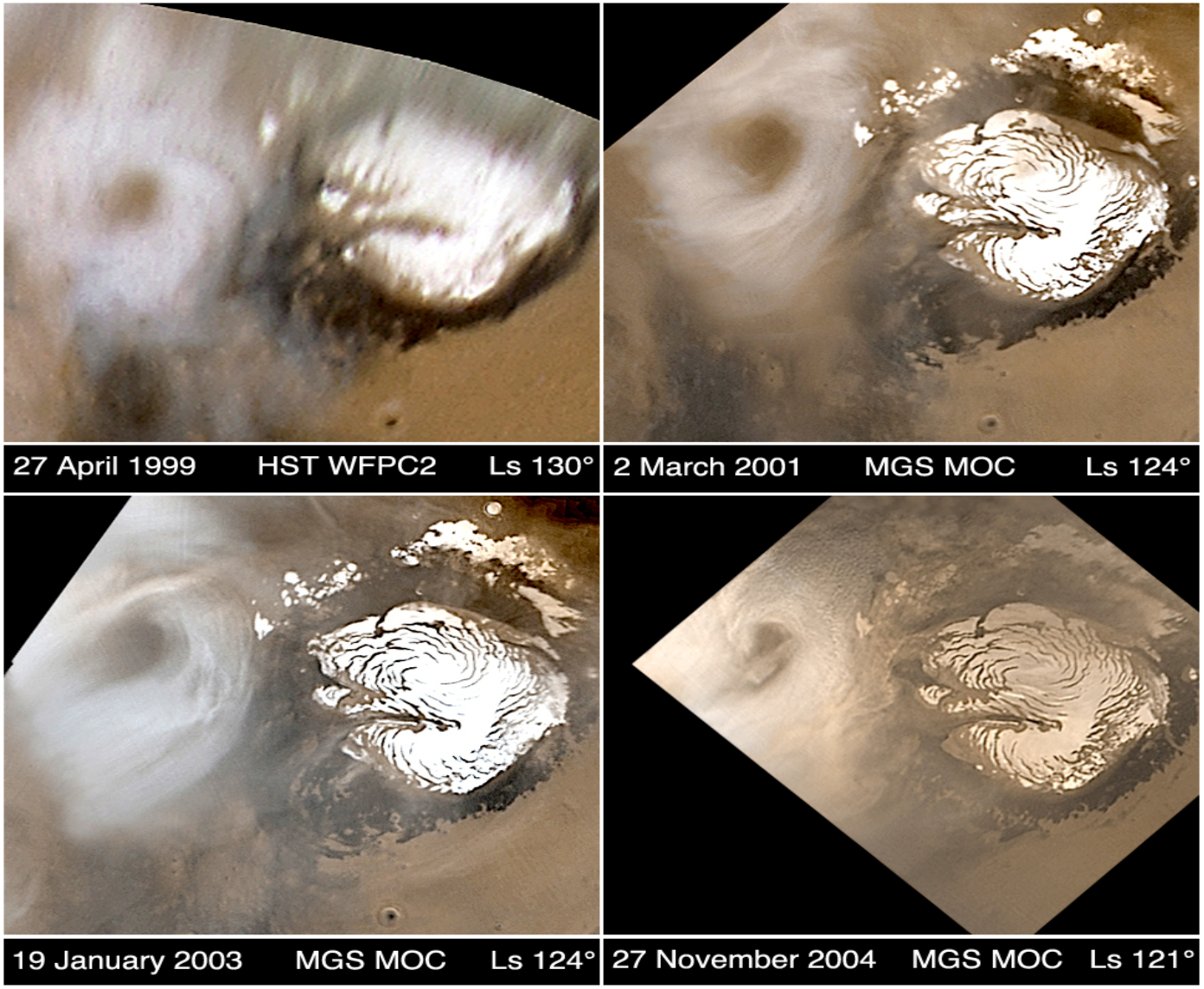
- Lessner D.J. Et al , PNAS, Nov 21, 2006 Vol 103 : “An unconventional pathway for reduction of CO2 to methane in CO-grown Methanosarcina acetivorans revealed by proteomics”.
- ABSTRACT:
- Methanosarcina acetivorans produces acetate, formate, and methane when cultured with CO as the growth substrate, which suggests novel features of CO methabolism. …The result indicate that oxidation of CO to CO2 supplies electrons for reduction of CO2 to a methyl group by steps and enzymes of the pathway for CO2 reduction determined for other methane producing species….

conclusions

- Questions:
- 1-ARE WE OBSERVING THE LOSS FROM THE POLAR CAP OF THE CO THAT SUBSTAINS LIFE IN THE ICE?
- ALTERNATIVELY
- 2- IS THE REACTION IN EQ.1 POSSIBLE WITHOUT LIFE, BUT WITH ENERGETIC PARTICLES BOMBARDMENT?
- Note : anomalous behaviour of CO is not observed in northern spring, but only in northern summer (sublimating remnant polar cap).

- THE END

Polar clouds



Polar vortex(?) close to the North pole, in northern summer,but displaced from it.

Top left Hubble image, the others MOC images.

Photochemistry in a pure CO_2 atmosphere

$$CO_2 + h\nu \rightarrow CO + O$$

$$\underline{O + O + M \rightarrow O_2 + M}$$

$$2CO_2 \rightarrow 2CO + O_2$$

$$O_2 + h\nu \rightarrow O + O$$

$$O_2 + O + M \rightarrow O_3$$

CO_2 stability problem

Prediction:	Observation:
CO: 7.72e-2	CO: 7.0e-4
O_2: 3.87e-2	O_2: 1.3e-3
O_3: 126DU	O_3: < a few DU

Something converts these components back to CO_2? (DU = Dobson Units)

HO_x catalytic chemistry

[McElroy & Donahue, 1972; Parkinson & Hunten, 1972]

$$H_2O + h\nu \rightarrow H + OH$$

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$\underline{O + HO_2 \rightarrow O_2 + OH}$$
$$CO + O \rightarrow CO_2$$

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_3 \rightarrow OH + O_2$$
$$\underline{O + O_2 + M \rightarrow O_3 + M}$$
$$CO + O \rightarrow CO_2$$

$$2(CO + OH \rightarrow CO_2 + H)$$
$$2(H + O_2 + M \rightarrow HO_2 + M)$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
$$\underline{H_2O_2 + h\nu \rightarrow 2OH}$$
$$2CO + O_2 \rightarrow 2CO_2$$

HOx-NOx catalytic chemistry

$$2(CO + OH \rightarrow CO_2 + H)$$
$$2(H + O_2 + M \rightarrow HO_2 + M)$$
$$HO_2 + NO \rightarrow NO_2 + OH$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + HO_2 \rightarrow O_2 + OH$$
$$2CO + O_2 \rightarrow 2CO_2$$

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow NO_2 + OH$$
$$NO_2 + O \rightarrow O_2 + NO$$
$$CO + O \rightarrow CO_2$$

Heterogeneous chemistry