SUPPORT ONLINE MATERIAL (SOM)

1- **MIXING RATIO DEFINITION AND UNITS.**
2- **SIGNAL TO NOISE RATIO FOR PFS MEASUREMENTS**
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1 - MIXING RATIO DEFINITION AND UNITS.

The volume mixing ratio, or simply mixing ratio, of a gas is defined as the ratio of the number density of the gas (i.e. number of molecules per unit volume) to the total number density of the atmosphere. Therefore, a CH_4 mixing ratio of 10^{-8} means that the number density of CH_4 is 10^{-8} times the total number density of the atmosphere. Following standard convention in earth's troposphere/stratosphere, this mixing ratio is expressed as 10 ppbv (parts per billion by volume). The mixing ratio is sometimes computed also by mass, in which case the common usage is mass mixing ratio. Mixing ratio is thus a dimensionless quantity.

2 - SIGNAL TO NOISE RATIO FOR PFS MEASUREMENTS

The PFS instrument aboard Mars Express is an infrared interferometer which consists of two channels, the long-wavelength channel (LWS, between 222 and 2000 cm^{-1}) and the short-wavelength channel (SWS, between 1600 and 8200 cm^{-1}). Its spectral resolution, as measured from the spectrum of a monochromatic mercury lamp, is 1.3 cm^{-1} without apodization. The PFS instrument is fully described in (*1*), and a comparison of its performance with the ISO-SWS spectrum of Mars (*2*) is discussed in (*3*). A complete description of the calibration procedures used for the PFS-SW channel is given in (*4*).

The radiometric and spectral calibration of the PFS SWS channel was achieved first in the laboratoy prior to the launch, then in space and, finally, when observing Mars. In-orbit calibration was achieved by taking spectra of the internal lamp, an internal blackbody and deep space. Laboratory measurements of the Noise Equivalent Radiation (NER) at room temperature have shown that the NER is minimum around 3000 cm^{-1} (0.045 $erg/s/cm^2/sr/cm^{-1}$), which is thus the most favorable spectral range for detecting minor constituents, and in particular the Q-branch of the strong ν_3 methane band. Measurements made in space with a cooled detector have confirmed this result (see figure SOM 1). From these measurements the NER at 3000 cm^{-1} at Mars is 0.010 $erg/s/cm^2/sr/cm^{-1}$. The measurements show a signal of the order of 0.32 $erg/s/cm^2/sr/cm^{-1}$, giving a SNR of 32 from a single measurement. Co-adding the spectra results in the lowering of the NER by a factor equal to the square root of the number of co-added spectra, or similarly, increasing the SNR by the same factor. Spectra integrated over a single orbit typically include 120 spectra (SNR of 352), while the total integrated spectrum shown in Fig.1 includes 1680 (2931) spectra (SNR of 1312 or 1512). The corresponding values of the NER at 3000 cm^{-1} are thus 0.00091 and 0.00024 (0.00018) $erg/s/cm^2sr/cm^{-1}$ respectively. These numbers correspond to the error bars shown in Figs.1, 3 and 4. The methane band shows on average a depth of 0.004 $erg/s/cm^2sr/cm^{-1}$, 16 times the NER.
The error on the quoted mixing ratio is due to NER (6%), to calibration of the spectrum (10 %), and to synthetic spectrum fitting (20 %). This corresponds to a global error of 36% that for a 10 ppbv mixing ratio becomes 3.6. We have rounded the uncertainty to a conservative 5 ppbv in order to allow for possible uncertainty in the vertical pressure–temperature profile.

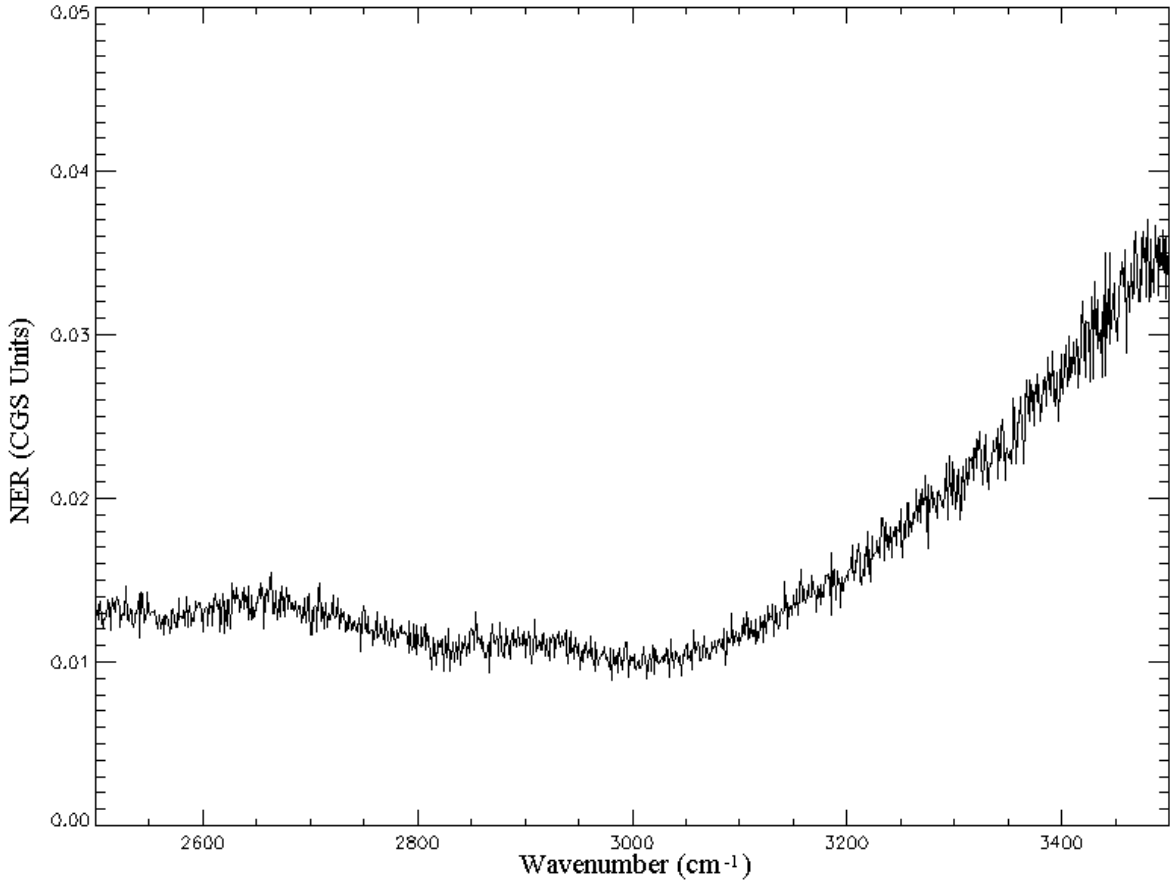


Figure caption . The Noise Equivalent Radiation (NER) of the PFS-SW channel as measured in space looking at deep space. The vertical unit is cgs unit (erg/s/cm^2/sr/cm^{-1}). The figure is a blow up of a similar figure from (*4*).

3 - COMPUTATION OF SYNTHETIC SPECTRA.

The spectrum of martian atmosphere is simulated with the traditional line-by-line approach, where the starting point is the database of the parameters of spectral lines of atmospheric gases, in particular, HITRAN database (http://www.hitran.com). Line parameters are adjusted to the conditions of martian atmosphere (temperature profile and ground pressure), and the contributions from individual lines are summed to give the monochromatic gaseous opacity spectrum. The gaseous opacity, together with the absorption and scattering properties of atmospheric aerosols, is the input to a numerical code that solves the equation of radiative transfer in the atmosphere with boundary conditions: incident solar flux at the top of the atmosphere and the lambertian surface albedo at the bottom. The surface albedo is assumed constant in the wavenumber range considered and it is adapted to the observed value. The solar spectrum is compiled on the basis of ATMOS observations reduced to the PFS spectral resolution. The martian atmospheric aerosols are also included. The aerosols are composed of dust and water ice clouds. The models describing the aerosols are empirical and are based on the previous observations. The monochromatic radiance spectrum is then convoluted with the spectral response function of the spectrometer to finally yield the synthetic spectrum that is compared with the measurements.
The details of the radiative transfer computations, thermal structure and cloud models, the solar flux, and the spectrometer characteristics used in the simulations presented can be found in the papers by Ignatiev et al., by Grassi et al., by Fiorenza and Formisano, and by Giuranna et al. to be published in a special issue of the *Planetary and Space Science* devoted to the first results obtained with the PFS (to be published in 2005). Here we add only that the normal composition of the martian atmosphere, i.e. CO_2 , CO, H_2O, and aerosols, is assumed for the synthetic spectra computation. The abundance of water vapor is adjusted to improve the fitting of the measured spectrum. Methane is included in the synthetic spectra to determine the presence and abundance of methane in martian atmosphere.

4. CALCULATION OF COMET SIZE VS. TIME IN THE PAST WHEN IMPACT OCCURRED, TO RESULT IN 10 ppbv OF METHANE TODAY

Calculation of comet size vs. time in the past when impact occurred

Assumptions:
1. The cometary impact delivered methane in a quantity that declines to the present day mixing ratio of 10 ppbv in the atmosphere of Mars.
2. For illustration, a methane lifetime of $2x10^{10}$ s near the surface is taken, but calculations are done for different assumed lifetimes of methane as the lifetime can vary (see text).
3. Methane is assumed to be 1% by weight of the comet, and the comet density is assumed to be, $\rho = 10^3$ kg m^{-3}.

Formulation of the problem:
Methane volume fraction, $f_v = 10^{-8}$, so that (1)
Methane mass fraction, $f_m = f_v\,(m_{CH4}/m_{CO2}) = 3.64x10^{-9}$ (2)
with molecular weights, $m_{CH4} = 16$, and $m_{CO2} = 44$, and the atmospheric mass as being mainly due to CO_2.
Hence, the mass of 10 ppbv of methane in the atmosphere of Mars, is
$M^M_{CH4} = f_m\, M_{CO2} = 3.64x10^{-9}\, p_{CO2}\, A_M/g_M$ (3)

where
$A_M = 4\pi R^2$, is the area of Mars (4)
using, $R_M = 3.393 \times 10^6$ m, $g_M = 3.72$ $m^2 s^{-1}$, $p_{CO2} = 6 \times 10^2$ Pa for Mars, we obtain,
$M^M_{CH4} = 8.49 \times 10^7$ kg, or approximately 8.5×10^4 tons of methane on Mars, with 10 ppbv CH_4.

If the cometary impact occurred today, it must deliver as much methane as there is in the atmosphere today, i.e. ~ 8.5×10^4 tons. Since, the methane mass fraction in the comet is taken 1%, the comet must have a mass 100 times greater. We call this mass M_C, so that

$M_C = 10^2 M^M_{CH4}$ (5)

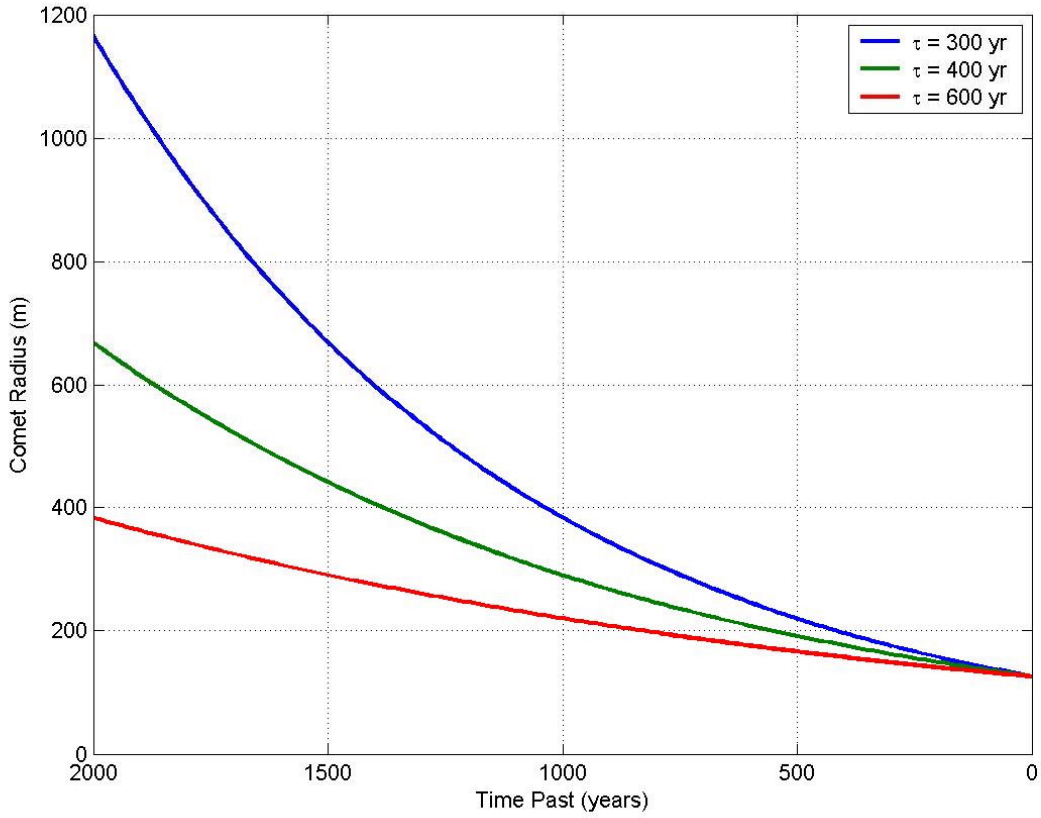
And, if the impact occurred at time T in the past, the comet mass should be:

$M_C(T) = \exp(T/\tau) M_C$, where τ is the assumed methane lifetime. (6)

The radius of such a comet (in meters) would then be:

$R(T) = [(3/4\pi) \exp(T/\tau) \rho^{-1} M_C]^{1/3}$, or (7)
$R(T) = [(3/4\pi) \exp(T/\tau) \rho^{-1} 10^2 f_v (m_{CH4}/m_{CO2}) p_{CO2} A_M/g_M]^{1/3}$ (8)

The results of the above calculations are plotted in the accompanying figure, assuming a methane lifetime of 300 yr, 400 yr, and 600 yr. The figure shows the radius of comet (ordinate) vs. time in the past when impact occurred (abscissa), with the constraint that the methane delivered at the time of impact declines to the present mixing ratio of 10 ppbv.



References and notes

(1) V. Formisano, F. Angrilli, G. Arnold, S. Atreya, G. Bianchini, D. Biondi et al.:The Planetary Fourier Spectrometer (PFS) on-board the european Mars Express mission Submitted to Planetary and Space Science, 2004a

(2) E. Lellouch, T. Encrenaz, T. de Graauw, S. Erard, P. Morris, J. Crovisier et al. :The 2.4-45 μm spectrum of Mars observed with the Infrared Space Observatory Planetary and Space Science, 48, 1393-1405, 2000

(3) V. Formisano, T. Encrenaz, S. Fonti, M. Giuranna, D. Grassi, H. Hirsch et al.:A Martian PFS average spectrum : Comparison with ISO-SWS .Submitted to Planetary and Space Science, 2004b

(4) M. Giuranna, V. Formisano, D. Biondi, A. Ekonomov, S. Fonti, D. Grassi et al.: Calibration of the Planetary Fourier Spectrometer Short Wavelength Channel. Submitted to Planetary and Space Science, 2004

(5) C. Fiorenza and V. Formisano, A solar spectrum for PFS data analysis, submitted to Planet. Space Sci. (2004).