

CO₂ ISOTOPES ON MARTIAN ATMOSPHERE FROM PLANETARY FOURIER SPECTROMETER (PFS-MEX) DATA.

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Introduction:

The stable isotope record contained within carbon and oxygen on Mars may provide important constraints regarding the origin of the planet and its relationship to that of other bodies in the Solar System, especially the Earth. Stable oxygen isotopes are particularly useful in the study of Mars because oxygen is abundantly present in both the Martian atmosphere and lithosphere. In particular it is present in CO₂, the main constituent (95%) of the atmosphere.

Despite their important roles, the precise O and C isotope compositions of Mars' atmosphere remain poorly known and both measurement and interpretation are difficult. Groundbased and spacecraft studies of CO₂ established for ¹²C/¹³C and ¹⁸O/¹⁶O values similar to that of the Earth (the "terrestrial" value) within various uncertainties (Kaplan et al., 1969; Young, 1971; Maguire, 1977; Schrey, 1985; confirmed by Viking measurements reported in Nier and McElroy, 1977). The values reported for the Viking mass spectrometers are for high altitudes (120-180 km), and may not pertain to the bulk atmosphere. Maguire's results on oxygen are based on the goodness of general fits. Earth-based estimates of ¹⁸O/¹⁶O show a lighter value (Eiler et al., 2000). Other values found from ground-based observations include those of Bjoraker et al. (1989) on oxygen in water, and Krasnopolsky (1996).

Here we report detection and preliminary analysis of the oxygen and carbon isotopes in CO₂ in the Martian atmosphere from the data returned by the Planetary Fourier Spectrometer (PFS) on board the Mars Express satellite.

Data:

The PFS instrument is a Fourier spectrometer that measures the infrared radiation emerging from the atmosphere and surface of Mars in the spectral range between 250 and 8200 cm⁻¹. The radiation field is analysed separately in two channels: the long-wavelength channel (LWC) covers the thermal infrared region between 250 and 1700 cm⁻¹ while the short-wavelength channel (SWC) measures the incoming Solar radiation, between 1700 and 8200 cm⁻¹, reflected by the surface; with a thermal part dominating below 2500 cm⁻¹. For both channels, spectral resolution is on the order of 1.3 cm⁻¹ for non-apodized spectra, sampled with a 1 cm⁻¹ step.

Among PFS spectral range some CO₂ isotopic bands are present. In this work we have studied the main CO₂ absorption band centred at 667 cm⁻¹ (LWC), in which are observed many q-branches and the major of tree isotopic bands (in the SWC) centred at 2614 cm⁻¹.

Method:

For the identification of CO₂ isotopes an average of 2041 spectra has been used to reduce noise. This subset was selected by requiring a high surface temperature (around 280 K) to increase the signal, and was obtained for spectra

near local noon and near the subsolar latitude.

To derive CO₂ isotopes abundances, we compare observed spectra with models that we have computed.

Computation of synthetic spectra was performed using a line-by-line radiative transfer code, including both the thermal component and the solar reflected spectrum (Fiorenza, Formisano, 2005). Lines parameters have been taken from molecular database HITRAN 2004 (www.hitran.com). The adopted temperature-pressure profile has been retrieved from the observed average spectrum by implementation of an inversion method applied to the main CO₂ absorption band centred at 667 cm⁻¹.

Methodological problems:

- There may be some ambiguities caused by using averaged spectra. Non-homogeneous conditions associated with different positions and times may give physically inconsistent results if an averaged spectrum is used to retrieve the atmospheric profiles.
- The radiative transfer solution is not unique, in the band under consideration (centered at 667 cm⁻¹), for retrieving thermal profile and isotopic abundances at the same time. However, once appropriate initial conditions are selected, this problem may become second order.
- Nominal PFS instrumental function has been used to convolve synthetic spectra. Discrepancies from this function in the LWC should anyway be checked and may provide some misfit in lines.
- Difficulties related to scattering in SWC (thermal and solar region) may provide problematic definitions of the continuum.

We now present the preliminary results of our analyses of the two channels, updated results will be presented at the conference.

Results:

In this section we show the two best fits obtained in both channels.

Long Wavelength Channel.

In figure 1 we present the average spectrum.

All the 8 CO₂ isotopes have been identified in the spectrum, by comparison with synthetic spectra and lines positions derived from HITRAN 2000. The PFS resolution is sufficient to resolve the Q-branches.

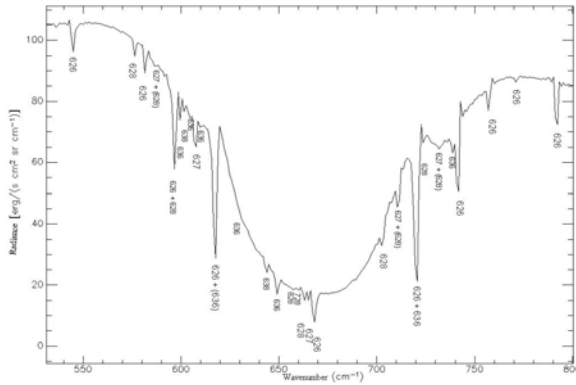


Figure 1. Identification of the CO₂ isotopes. ¹⁶O¹²C¹⁷O is named 627, the same for the other isotopes.

In figure 2 is shown the best global fit of the band obtained in this channel.

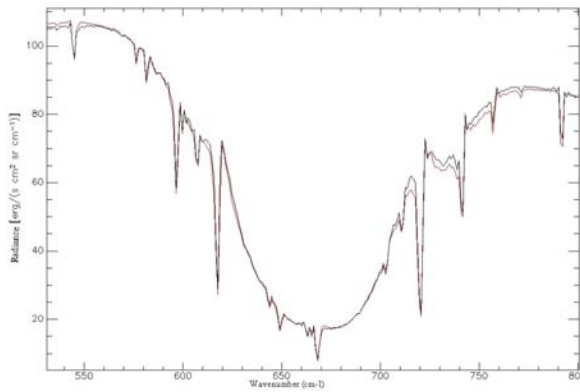


Figure 2. Global fit of the main CO₂ band: in black average spectrum, in red synthetic.

In figures 3,4,5,6 we present the fit of the tree isotopes 628, 636 and 627.

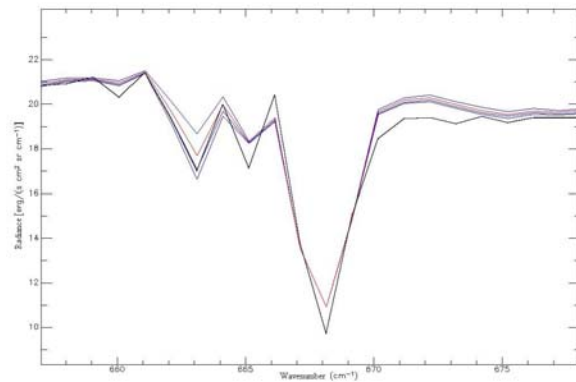


Figure 3. Isotope 628 at 663 cm⁻¹: blow up of the center of the band. In black average spectrum, in red and blue synthetic spectra with respectively 1, 0.5, 1.5 terrestrial values.

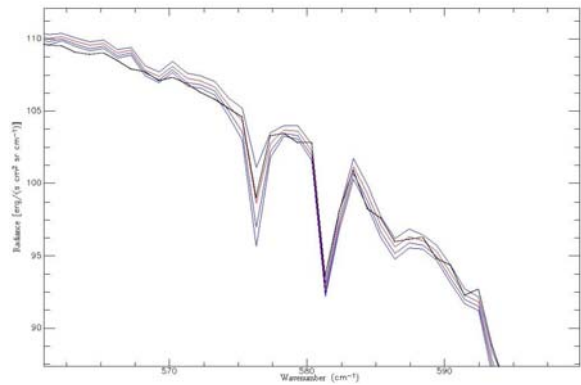


Figure 4. Isotope 628 at 576 cm⁻¹. In black average spectrum, in red and blue synthetic spectra with respectively 1, 0.5, 1.5 terrestrial values.

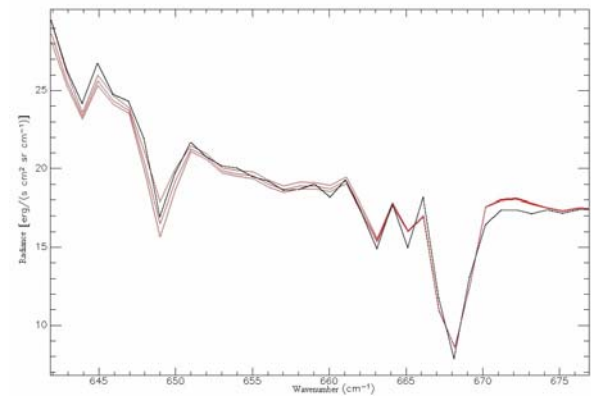


Figure 5. Isotope 636 at 649 cm⁻¹: blow up of the center of the band. In black average spectrum, in red synthetic spectra with respectively 1, 0.5, 1.5 terrestrial values.

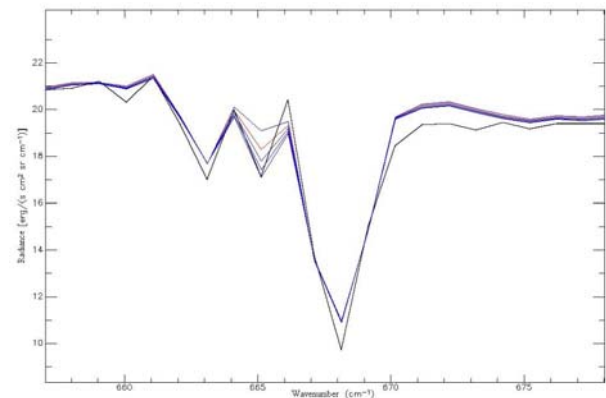


Figure 6. Isotope 627 at 665 cm⁻¹: blow up of the center of the band. In black average spectrum, in red and blue synthetic spectra with respectively 1, 0.5, 1.5, 2, 2.5 terrestrial values.

Short Wavelength Channel.

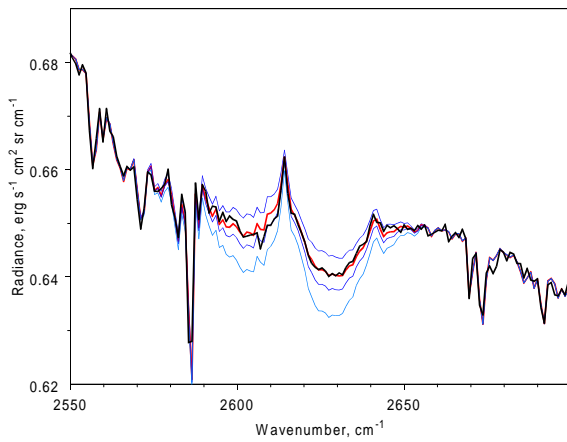


Figure 7. CO₂ 628 isotopic band centred at 2614 cm⁻¹: in black colour — average spectrum, in red colour — synthetic spectrum for the best fit value of 0.84 (±20%) of the terrestrial abundance; for reference blue curves show synthetic spectra for CO₂ 628 abundances of 0, 0.5, 1, and 1.5 terrestrial values..

In figure 7 we present a fit of the isotopic band centred at 2614 cm⁻¹. The band is mainly due to 628 isotope, but in the right side also the 627 isotopic band centred at 2641 cm⁻¹ gives a contribute.

Considering just the fit on the left side we can observe a value similar or smaller then terrestrial one.

For terrestrial values we have assumed the values reported in HITRAN 2004.

From these fits we can find the results:

Molecule	Abundance (x Earth value)
636 (649 cm ⁻¹)	~1
628 (576 cm ⁻¹)	~1
628 (663 cm ⁻¹)	~1.5
627 (665 cm ⁻¹)	~2.5
628 (2614 cm ⁻¹)	~1

Conclusions:

In these preliminary observations there are some discrepancies between the observed abundance of 628 isotope at different wavelenghts: at 576 and 2614 cm⁻¹ is similar to the terrestrial value (or less), while in the bottom of the band (663 cm⁻¹) it is found to be ~1.5.

From the last spectral range the 627 isotope seems to have much higher abundance than terrestrial value.

Interpretation of the data remains anyway problematic. Possible future improvements may consist in selecting spectra to be averaged on more homogenous basis and to develop better methods for continuum definition. Definition of instrumental function and calibration of the data will be likely subject to further improvements. The actual situation does allow to rule out terrestrial values for the CO₂ isotopes.

References:

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