

# MEASURING THE $^{13}\text{C}/^{12}\text{C}$ IN $\text{CO}_2$ IN THE LOWER ATMOSPHERE OF MARS WITH NOMAD/TGO: CHALLENGES AND INTERPRETATION

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## Introduction:

The two infrared spectrometers onboard the ExoMars Trace Gas Orbiter (TGO) spacecraft, the Atmospheric Chemistry Suite (ACS) and the Nadir and Occultation for Mars Discovery (NOMAD) have been providing observations since April 2018 that are a unique source of information to unveil the vertical structure of the atmosphere of Mars in a level of detail never previously seen. In this work, we focus on understanding how the NOMAD data can be useful to constrain the isotopic composition of C in  $\text{CO}_2$ . This has been measured on several occasions on the surface [1], and in near-surface atmospheric samples [2,3], and is of great interest as  $\text{CO}_2$  is the main C reservoir in the atmosphere of Mars, allowing to trace the history of atmospheric loss and differences with other inner solar system bodies. Additionally, proper characterization of the uncertainties of derived isotopic ratios is a very important proxy towards a better understanding of the instrument limitations and performances.

## Data and analysis:

NOMAD is a 3-channel spectrometer working in the spectral ranges 0.2-0.65  $\mu\text{m}$  (UVIS channel) and 2.2-4.3  $\mu\text{m}$  (SO and LNO channels). The data taken by the Solar Occultation (SO) channel measurements in the infrared channel is used in this work. SO is an echelle grating spectrometer with relatively high spectral resolution ( $\lambda/d\lambda \sim 17,000$ ), and an Acousto Optical Tunable Filter (AOTF) used to instantaneously switch the observed diffraction orders, with a typical cycle of 1 second. This yields a vertical sampling of less than 1 km from the surface to 250 km of altitude. While typically NOMAD cycles through 5 or 6 diffraction orders at every occultation, this setup is often not adequate to measure  $^{13}\text{C}/^{12}\text{C}$ . Expected differences between this isotopic ratio on Earth and the one on Mars are indeed very small ( $< 0.1$ , or equivalently 100‰), therefore it is important, when attempting to measure it, to pinpoint the other parameters that can create a bias in the measured isotopic ratio. Because each diffraction order measured by NOMAD covers only a limited number of spectral lines with similar degrees of saturation, and mostly similar temperature dependencies, the most effective way to quantify simultaneously the temperature,  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  is to choose numerous diffraction

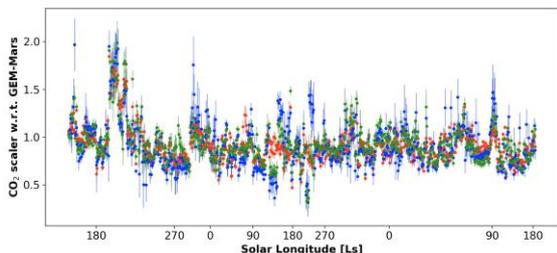
orders measured simultaneously, with spectral lines with similar degrees of saturation. For these reasons, the data we use in this work are the Full Scan data, where a large set (or all) of diffraction orders are acquired at a few altitudes. Despite the very coarse vertical sampling (3 to 25 km), these scans allow to collect data in several diffraction orders that are not measured frequently, maximizing the information gathered for  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$  and temperature. For this work, we have used full scans acquired between Apr/2018 ( $L_S \sim 160$  MY34) and Dec/2021 ( $L_S \sim 137$  MY36), in particular the spectra from orders 141 (3170-3200  $\text{cm}^{-1}$ ), 145 (3255-3285  $\text{cm}^{-1}$ ), 146 (3278-3308  $\text{cm}^{-1}$ ), and 148 (3332-3363  $\text{cm}^{-1}$ ), for a total of  $\sim 2700$  spectra per order. From order 148 the average rotational temperature along the line of sight can be derived with an accuracy of about 5 K [4], which then can be used to derive the column density at a specific tangent altitude of  $^{12}\text{CO}_2$  (order 141) and  $^{13}\text{CO}_2$  (orders 145 and 146). In all these orders, various lines with different J are present, providing proper constraints on the abundances of the two isotopes. The accuracy of the retrievals is also possible thanks to recent calibration efforts for the AOTF transfer function and the ILS of the SO channel, which are fully parameterized with the diffraction order [5]. Retrievals are performed using the Planetary Spectrum Generator (PSG, [6,7]), a full general purpose radiative transfer code, which contains a dedicated retrieval module based on Optimal Estimation and is configured with all the instrumental parameters of NOMAD SO natively accounted for. The use of diffraction orders that are close in frequency minimizes altitude biases, as all the orders will be simultaneously acquired within  $\sim 200$  meters, effectively obtaining well collocated measurements.

The intensity of the lines in the observed orders are particularly suitable to obtain meaningful values for the C isotopic ratio in the interval between 10 and 50 km in altitude. Below 10 km, the combination of the atmospheric opacity and line saturation will degrade the accuracy, while above 50 km the Signal-to-Noise Ratio (SNR) of the lines will be too low to obtain significant values.

## Results and discussion:

Once all the retrievals are completed, we filter the values by excluding values with low SNR and those spectra where the intensity of the spectral lines is smaller than 5 times the radiometric noise. Once a

stringent selection is done, a total of ~2000 isotopic ratio single values are selected. **Figure 1** shows the

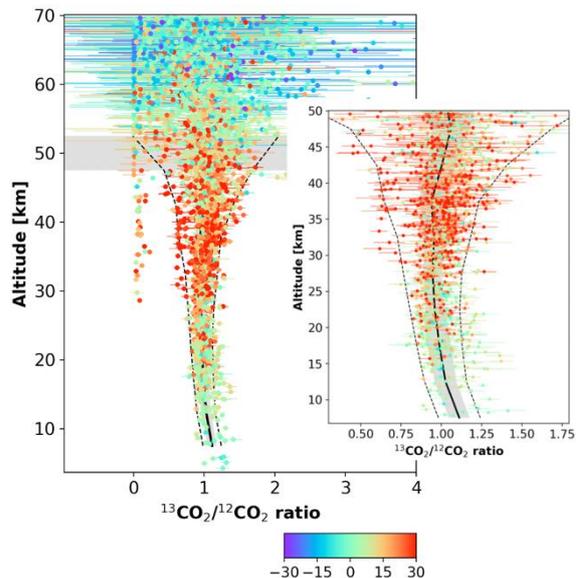


**Figure 1.** Temporal series of the retrieved values of  $^{12}\text{CO}_2$  (red, from order 141), and the  $^{13}\text{CO}_2$  (order 145 and 146, blue and green respectively). Enhancements of both isotopes due to the GDS can be seen at the beginning of the series.

temporal series of the retrieved values of the two isotopes of  $\text{CO}_2$  in terms of scaler of the density as prescribed by co-located GEM model profiles [8]. The abundance of the two isotopes with respect to the GEM model are the same within the dispersion of the points, and we see that the  $\text{CO}_2$  density is for both isotopes enhanced during the dusty season (in particular the GDS during MY34). There does not appear to any significant variability of the C isotopic ratio with location, season, and atmospheric state. However, because of the limited temporal coverage, it is difficult to derive specific seasonal trends. The most significant product of this dataset is an average vertical profile of the C isotopic ratio. This is shown in **Figure 2**, together with the full set of valid points. The color of each point represents the difference between the temperature as given by GEM and the one derived using the data of order 148. A value of on the x-axis equal to one means that the measured isotopic ratio is equivalent to the Earth Vienna Pee Dee Belemnite (VPDB) for carbon,  $^{13}\text{C}/^{12}\text{C} = 1.123 \times 10^{-2}$ ). The single points show no significant trend in terms of temperature vs. isotopic ratio, meaning that the information about temperature and the abundances of the two isotopes are independent of each other.

The observed dispersion in the single values increases with altitude because the SNR of the spectral lines decreases. One of the most important questions to assign the correct uncertainty to the average  $^{13}\text{C}/^{12}\text{C}$  at each altitude is the determination of whether the observed dispersion in the single spectrum results is of stochastic nature, meaning that it is not dominated by systematics, rather it is related to the limitations of the instrument and the accuracy of spectroscopy. To answer this question, we have conducted a specific analysis that quantifies the expected uncertainty of a single measurement depending on the observed column of  $\text{CO}_2$  and the prescribed radiometric noise. By using the simulated curve of growth of the lines of the two isotopes in the observed orders, we compare the median of the trans-

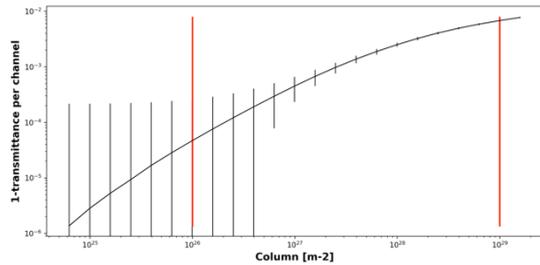
mittances across an order as they vary with the  $\text{CO}_2$  column with the radiometric noise, as seen in **Figure 3**.



**Figure 2.** Full set of retrieved values of  $^{13}\text{C}/^{12}\text{C}$  (x-axis, 1 meaning VPDB standard) as a function of the altitude (y-axis) and related error bars. The color of each point represents the retrieved difference in temperature along the line of sight with respect to the GEM model. The expected dispersion of the points as derived from the analysis of the curve of growth (see text and Figure 3) is shown by the dashed lines.

This allows, for every column amount of  $\text{CO}_2$  (namely, a certain altitude), quantification of the uncertainty in the derived column as related to the saturation of the lines (spectroscopic limitations) and the instrument limitations (resolving power, continuum effects). It can be clearly seen that the uncertainty diverges for columns below the one corresponding to an average altitude of 50 km, consistent with the observed spread of the points in **Figure 2**. This analysis enables quantification of the expected dispersion of  $^{13}\text{C}/^{12}\text{C}$ , which is also reported in **Figure 2**.

The fact that more than 90% of the points, at every altitude, fall within the derived 3-sigma error from the analysis of the curve of growth justifies the fact that the observed spread of the points can be treated in a stochastic fashion, meaning that averaging several measurements to achieve higher precision is possible. By doing that, we quantify the isotopic ratio in the lower atmosphere (10-25 km) is  $1.027 \pm 0.030$  VPDB, largely consistent with the value observed by MSL in surface minerals and the atmosphere. The value is fairly constant throughout the atmosphere with oscillations within the error bars. Upper atmosphere values (>50 km) do not show any inconsistency with the values reported using ACS observation above 60 km [9].



**Figure 3.** Simulated curve of growth for the  $^{13}\text{CO}_2$  lines in order 146. The x-axis shows the column amount of  $\text{CO}_2$  along the line of sight, while the y-axis shows the average transmittance across the order (net of the median of the transmittance, to account for the continuum effects). The vertical error bars correspond to the radiometric noise scaled by the number of pixels (320 for SO), and the red lines correspond to the average column at 5 and 65 km of altitude.

### Conclusions:

Observations by NOMAD have been used to measure an average vertical profile of the  $\text{CO}_2$  C isotopic ratio in the lower atmosphere of Mars. The isotopic ratio shows no significant seasonal or altitudinal trends. Besides the values reported in this work, this analysis has explored the main instrumental factors limiting the precision of the measurement. We conclude that the precision of the measurement is essentially limited by the radiometric SNR, and by the precision with which the spectral continuum is quantified, which plays an essential role when spectral lines are close to the saturation. If several lines (namely, several diffraction orders) are used in the analysis, the accuracy of the atmospheric temperature is not the main limiting factor.

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