

MULTI-INSTRUMENT AND MULTI-APPROACH CARBON ISOTOPIC STUDIES ON MARS G. Liuzzi¹, G. L. Villanueva², S. Faggi^{2,3}, S. Aoki^{4,5}, S. W. Stone², G. Masiello¹, C. Serio¹, and the NOMAD team. ¹Scuola di Ingegneria, Università degli Studi della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza (PZ), Italy, giuliano.liuzzi@unibas.it, ²NASA Goddard Space Flight Center, 8800 Greenbelt Rd., 20771 Greenbelt, MD, USA, ³American University, 4400 Massachusetts Avenue, 20016 Washington DC, USA, ⁴Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan, ⁵Royal Belgian Institute for Space Aeronomy, 3 Avenue Circulaire, 1180 Brussels, Belgium.

Introduction: The understanding of planetary evolution benefits of several kinds of measurements, among which the analysis of the isotopic composition of its main constituents is certainly one of the most effective [1], [2]. In this context, though, several processes can affect the isotopic composition of surface materials and atmospheric gases, and this needs to be taken into account in the interpretation of those measurements. While the average (the “bulk”) value of isotopic abundances can tell the story of long-term evolution, localized measurements and their spatial-temporal variability is important to better constrain current fractionation and escape processes, which can also affect in different way more than one gaseous species through, e.g., photochemistry. The most recent measurements of carbon isotopic composition from ground on Mars [3]–[5] are yet to be reconciled with the atmospheric ones [6], [7], which show some discrepancy both in absolute value and variability. In this work, we focus on this particular aspect, showing the recent progress made in characterizing carbon isotopic composition in atmospheric CO₂ and CO using data from the ExoMars Trace Gas Orbiter (TGO) Nadir and Occultation for Mars Discovery instrument (NOMAD [8], [9]). In addition, we show that a possible way to unveil the true bulk carbon isotopic composition is to derive it from CO₂ ices at the Poles through spectroscopic measurements of ice reflectance at high resolution.

Data and methods: On the atmospheric side, we have collected all NOMAD observations in Solar Occultation (SO) Geometry, which allows for the observation of the vertical structure of the atmosphere at very high vertical sampling (<1 km in most cases) at very specific locations. Within the course of 2 months, these observations cover most latitudes and thus enable global mapping of the properties of several atmospheric constituents. Each occultations lasts only a few minutes, yet can be made up of 50 to >1000 spectra, depending on the angle between the orbit and the surface. NOMAD is a grating spectrometer covering the spectral interval 2.2–4.3 μm, yet at each occultation it observes a specific set of diffraction orders, each one covering a narrow spectral interval (20–35 cm⁻¹), selected through a specific filter called the AOTF. The spectral response of the AOTF is quite complex, and

together with the ILS and other properties of the SO channel, it has been exhaustively characterized and documented [10], [11]. In this work we use NOMAD Full Scan data to gather appropriate information about ¹²C, ¹³C and temperature. We use full scans acquired between Apr/2018 (*L_S* ~160 MY34) and Dec/2021 (*L_S* ~137 MY36), a type of data in which many diffraction orders are measured along the vertical. From these we derive the average rotational temperature along the line of sight with an accuracy of about 5 K [12], which then can be used to derive the column density at a specific tangent altitude – in particular - of ¹²CO₂ and ¹³CO₂. Another set of specific NOMAD diffraction orders has been used instead to retrieve the carbon isotopic fractionation in atmospheric CO [13], [14]. The two results allow to understand the current interplay between these two species and to characterize their variability in the middle atmosphere of Mars (20–40 km of altitude). As far as the surface is concerned, we have evaluated the possibility of retrieving the ¹²CO₂ and ¹³CO₂ ice abundances in seasonal deposits in the Southern Polar Cap using data from the Mars Express SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars (SPICAM [15], [16]) and used a selected dataset to evaluate the feasibility and sensitivity of such analysis, by identifying potential features especially for ¹³CO₂ ice, which are currently undocumented in literature. For our analyses, we have used the Planetary Spectrum Generator (PSG, [17], [18]), 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 and SPICAM.

Results: By an in-depth analysis of the NOMAD full scan data, we find that atmospheric CO₂ in the middle atmosphere is depleted in ¹³C compared to the Earth standard by 30‰ to 45‰, in line with past ground-based measurements and yet in contrast with the value obtained by Curiosity (46±4‰). We argue that this means that the value measured by Curiosity may not be representative of the whole atmosphere, and that an atmosphere slightly depleted in ¹³C may be more consistent with many other data acquired by analyzing surface mineral samples. We see that there is no evident indication of temporal variability on a seasonal

timescale of this isotopic ratio, yet NOMAD data do not reveal any subtle variability on short timescales. The discrepancy with MSL Curiosity measurements remains a point of discussion, but one possible explanation that goes beyond the lack of collocation between TGO and MSL measurements is the possibility that surface-atmosphere interactions near the surface alter the isotopic composition of CO₂ on a daily timescale, and that this effect is practically null above 1 km of altitude. As for SPICAM, we demonstrate the existence of bright, detectable ¹³CO₂ ice features, and discuss their behavior with the physical properties of the observed surface ice. We also discuss the importance of adopting the correct physical model to describe the mixing of different surface components in radiative transfer, and show possible ways forward to retrieve the carbon isotopic composition of seasonal CO₂ ice with SPICAM, concluding that more lab measurements of its optical properties are much needed to have a solid base for retrievals.

References:

- [1] D. D. Bogard, R. N. Clayton, K. Marti, T. Owen, and G. Turner, “Martian Volatiles: Isotopic Composition, Origin, and Evolution,” *Space Science Reviews*, vol. 96, no. 1, Art. no. 1, Apr. 2001, doi: 10.1023/A:1011974028370.
- [2] H. Lammer, R. Brasser, A. Johansen, M. Scherf, and M. Leitzinger, “Formation of Venus, Earth and Mars: Constrained by Isotopes,” *Space Sci Rev*, vol. 217, no. 1, p. 7, Dec. 2020, doi: 10.1007/s11214-020-00778-4.
- [3] C. H. House *et al.*, “Depleted carbon isotope compositions observed at Gale crater, Mars,” *Proceedings of the National Academy of Sciences*, vol. 119, no. 4, Art. no. 4, Jan. 2022, doi: 10.1073/pnas.2115651119.
- [4] C. R. Webster *et al.*, “Isotope Ratios of H, C, and O in CO₂ and H₂O of the Martian Atmosphere,” *Science*, vol. 341, no. 6143, pp. 260–263, Jul. 2013, doi: 10.1126/science.1237961.
- [5] P. R. Mahaffy *et al.*, “The Sample Analysis at Mars Investigation and Instrument Suite,” *Space Science Reviews*, vol. 170, no. 1–4, pp. 401–478, Sep. 2012, doi: 10.1007/s11214-012-9879-z.
- [6] T. Encrenaz *et al.*, “Infrared imaging spectroscopy of Mars: H₂O mapping and determination of CO₂ isotopic ratios,” *Icarus*, vol. 179, no. 1, pp. 43–54, Dec. 2005, doi: 10.1016/j.icarus.2005.06.022.
- [7] J. Alday *et al.*, “Isotopic Composition of CO₂ in the Atmosphere of Mars: Fractionation by Diffusive Separation Observed by the ExoMars Trace Gas Orbiter,” *Journal of Geophysical Research: Planets*, vol. 126, no. 12, p. e2021JE006992, 2021, doi: 10.1029/2021JE006992.
- [8] A. C. Vandaele *et al.*, “NOMAD, an Integrated Suite of Three Spectrometers for the ExoMars Trace Gas Mission: Technical Description, Science Objectives and Expected Performance,” *Space Science Reviews*, vol. 214, no. 5, Aug. 2018, doi: 10.1007/s11214-018-0517-2.
- [9] E. Neefs *et al.*, “NOMAD spectrometer on the ExoMars trace gas orbiter mission: part 1—design, manufacturing and testing of the infrared channels,” *Applied Optics*, vol. 54, no. 28, p. 8494, Oct. 2015, doi: 10.1364/AO.54.008494.
- [10] G. Liuzzi *et al.*, “Methane on Mars: New insights into the sensitivity of CH₄ with the NOMAD/ExoMars spectrometer through its first in-flight calibration,” *Icarus*, vol. 321, pp. 671–690, Mar. 2019, doi: 10.1016/j.icarus.2018.09.021.
- [11] G. L. Villanueva *et al.*, “The Deuterium Isotopic Ratio of Water Released From the Martian Caps as Measured With TGO/NOMAD,” *Geophysical Research Letters*, vol. 49, no. 12, p. e2022GL098161, 2022, doi: 10.1029/2022GL098161.
- [12] G. Liuzzi *et al.*, “First Detection and Thermal Characterization of Terminator CO₂ Ice Clouds With ExoMars/NOMAD,” *Geophysical Research Letters*, vol. 48, no. 22, p. e2021GL095895, 2021, doi: 10.1029/2021GL095895.
- [13] S. Aoki *et al.*, “Depletion of ¹³C in CO in the Atmosphere of Mars Suggested by ExoMars-TGO/NOMAD Observations,” *Planet. Sci. J.*, vol. 4, no. 5, p. 97, May 2023, doi: 10.3847/PSJ/acd32f.
- [14] T. Yoshida *et al.*, “Strong Depletion of ¹³C in CO Induced by Photolysis of CO₂ in the Martian Atmosphere, Calculated by a Photochemical Model,” *Planet. Sci. J.*, vol. 4, no. 3, p. 53, Mar. 2023, doi: 10.3847/PSJ/acc030.
- [15] O. Korablev *et al.*, “SPICAM IR acousto-optic spectrometer experiment on Mars Express,” *J. Geophys. Res.*, vol. 111, no. E9, p. E09S03, 2006, doi: 10.1029/2006JE002696.
- [16] F. Montmessin *et al.*, “SPICAM on Mars Express: A 10 year in-depth survey of the Martian atmosphere,” *Icarus*, vol. 297, pp. 195–216, Nov. 2017, doi: 10.1016/j.icarus.2017.06.022.
- [17] G. L. Villanueva, M. D. Smith, S. Protopapa, S. Faggi, and A. M. Mandell, “Planetary Spectrum Generator: An accurate online radiative transfer suite for atmospheres, comets, small bodies and exoplanets,” *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 217, pp. 86–104, Sep. 2018, doi: 10.1016/j.jqsrt.2018.05.023.

- [18] G. L. Villanueva *et al.*, *Fundamentals of the Planetary Spectrum Generator*. 2022. Accessed: Jun. 07, 2022. ISBN: 978-0-578-36143-7.