

## Oxygen-18 Carbon Dioxide Isotope Ratio in Mars Atmosphere

Kostiuk, T.(1), T. A. Livengood(2), T. Hewagama(2), R. Smith (1), K. E. Fast(1), J. Annen(1), G. Sonnabend (3), and M. Sornig (3),

(1) NASA Goddard Space Flight Center, USA (2) University of Maryland and GSFC, USA (3) University of Köln, Germany

### Abstract

The determination of isotopic ratios on Mars is important to the study of atmospheric evolution [1]. The relative abundance of isotopes of CO<sub>2</sub> provides insight into the loss of Mars' primordial atmosphere. Isotopic ratios also provide markers in the study of geochemistry of Mars meteorites and future returned samples formed in equilibrium with ambient atmosphere, and are probes of biogenic and abiotic chemistry, which differ in isotope fractionation.

Due to its lesser gravity and relatively thin residual atmosphere, Mars' atmosphere should be enriched in heavy isotopes [1]. However Viking [2] results indicated an Earth-like singly substituted oxygen-18 CO<sub>2</sub> isotopic ratio, <sup>18</sup>OCO/OCO, with  $\delta^{18}\text{O} = 0 \pm 50\%$  relative to Vienna Standard Mean Ocean Water (VSMOW). By comparison, isotopic ratios in Earth atmospheric CO<sub>2</sub> are not uniquely defined due to seasonal and biotic variability, but have a range 0–41% relative to VSMOW [3, 4]. Phoenix lander TEGA [3] measurements found a modest enrichment of  $\delta^{18}\text{O} = 31.0 \pm 5.7\%$ . Only the Viking and Phoenix landers have carried a mass spectrometer to Mars, so far, until the arrival of Mars Science Laboratory in August 2012. Using ground-based spectroscopic techniques Krasnopolsky et al. [5] also found modest enrichment  $\delta^{18}\text{O} = 18 \pm 18\%$ .

We present results from fully resolved spectroscopic measurements near 10.6  $\mu\text{m}$  of both the normal and singly substituted oxygen-18 CO<sub>2</sub> lines, taken with the Goddard Space Flight Center Heterodyne Instrument for Planetary Winds And Composition (HIPWAC) at the NASA Infrared Telescope Facility on Mauna Kea, Hawaii. Measurements with

spectral resolving power  $\lambda/\Delta\lambda=10^7$  were obtained in October 2007 with an instantaneous field-of-view on the planet of  $\sim 1$  arcsec, at the locations shown in Fig. 1 as open squares. The solid and broken line tracks show Mars SPICAM measurements of ozone corresponding to ozone measurements also obtained with HIPWAC and shown as hatched and solid regions [6].

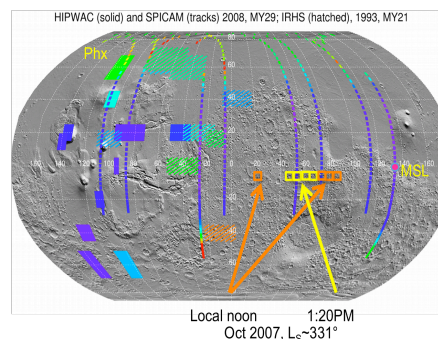


Figure 1: Locations of measured <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O fractional abundance on Mars (open squares). The colored tracks are Mars Express SPICAM measurements of ozone; the solid and hatched areas show contemporaneous HIPWAC measurements of ozone [6].

Figure 2 illustrates the CO<sub>2</sub> normal-isotope and O-18 isotopologue lines measured on Mars at  $\sim 1$  MHz (0.0003 cm<sup>-1</sup>) spectral resolution. The strong absorption line constrains the temperature simultaneously at the position of the measurement. The narrow mesospheric non-LTE line emission is also seen at the core of the absorption. The standard Mars Global Surveyor temperature profile was used to obtain the modeled emergent spectrum in blue. It clearly does not fit as well as the thermal profile retrieved from the CO<sub>2</sub> absorption line profile (red fit).

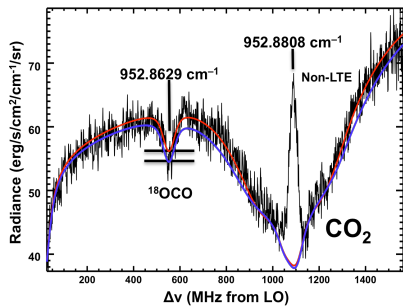


Figure 2: HIPWAC measurements of CO<sub>2</sub> spectrum on Mars near 10.5 μm. The broad absorption retrieves the temperature. The fitted model spectra correspond to using the standard MGS thermal profile (blue), and our retrieved profile (red). The fit to the isotopic line is excellent and yields  $\delta^{18}\text{O} = +9 \pm 14\%$ .

Radiative-transfer software developed in-house at GSFC to be compatible with very high spectral resolving power [7] was used to obtain the temperature profile and spectral fit. The fit on the 952.8629 cm<sup>-1</sup> <sup>18</sup>OC<sup>16</sup>O line retrieves  $\delta^{18}\text{O} = +9 \pm 14\%$ . There appears to be no significant enhancement in the average over the extended region measured. Additional, more global, measurements were acquired in May 2012 and these data are being analyzed.

These and additional high spectral resolution ground-based global measurements of  $\delta^{18}\text{O}$  can investigate Mars' atmospheric history; help define Mars Science Laboratory (MSL) protocols to sample isotopic ratios diurnally and seasonally, throughout its prime mission; and investigate possible meridional variability due to mass-fractionation in the polar freeze-sublimate cycle, similar to effects in terrestrial polar ice formation [8]. Such measurements would also complement results from future landers drilling into polar caps for isotopic insight into climatic history on Mars.

## Acknowledgements

Results of observations at the Infrared Telescope Facility (IRTF), operated by the University of Hawaii under Cooperative Agreement number

NCC 5-538 with the National Aeronautics and Space Administration, Science Mission Directorate, Planetary Astronomy Program. This work was supported by the NASA Planetary Astronomy Program.

## References

- [1] Fox, J. L., and A. Hać (2010). Isotope fractionation in the photochemical escape of O from Mars. *Icarus* **208**, 176–191, doi: 10.1016/j.icarus.2010.01.019.
- [2] Owen, T. (1992), The composition and early history of the atmosphere of Mars, in *Mars*, edited by H. H. Kieffer, B. M. Jakosky, C. W. Snyder and M. S. Matthews, pp. 818–834, University of Arizona Press, Tucson.
- [3] Niles, P. B., W. V. Boynton, J. H. Hoffman, D. W. Ming, and D. Hamara (2010). Stable Isotope Measurements of Martian Atmospheric CO<sub>2</sub> at the Phoenix Landing Site. *Science* **329**, 1334–1337, doi: 10.1126/science.1192863.
- [4] Francey, R. J., and P. P. Tans (1987). Latitudinal variation in oxygen-18 of atmospheric CO<sub>2</sub>. *Nature* **327**, 495–497, doi: 10.1038/327495a0.
- [5] Krasnopolsky, V. A., J. P. Maillard, T. C. Owen, R. A. Toth, and M. D. Smith (2007). Oxygen and carbon isotope ratios in the martian atmosphere. *Icarus* **192**, 396–403, doi: 10.1016/j.icarus.2007.1008.1013.
- [6] Fast, K. E., T. Kostiuik, F. Lefèvre, T. Hewagama, T. A. Livengood, J. D. Delgado, J. Annen, and G. Sonnabend (2009). Comparison of HIPWAC and Mars Express SPICAM observations of ozone on Mars 2006–2008 and variation from 1993 IRHS observations. *Icarus* **203**, 20–27, doi: 10.1016/j.icarus.2009.05.005.
- [7] Hewagama, T., J. Goldstein, T. A. Livengood, D. Buhl, F. Espenak, K. Fast, T. Kostiuik, and F. Schmülling (2008). Beam integrated high-resolution infrared spectra: Accurate modeling of thermal emission from extended clear atmospheres. *Journal of Quantitative Spectroscopy & Radiative Transfer* **109**, 1081–1097.
- [8] Craig, H., Y. Horibe, and T. Sowers (1988). Gravitational separation of gases and isotopes in polar ice caps. *Science* **242**, 1675–1678, doi: 10.1126/science.242.4886.1675.

