

Daily Variation of Heavy Carbon Dioxide in Mars Atmosphere

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Abstract

The atmosphere of Mars is significantly enriched in C and O heavy isotopes, detected by ground based high-resolution infrared spectroscopy as well as *in situ* measurements by the *Phoenix* lander and Mars Science Laboratory *Curiosity* rover. Heavy isotope enrichment is consistent with the preferential loss of light isotopes in eroding Mars' primordial atmosphere. Infrared spectroscopy of Mars collected in May 2012 as well as in March and May of 2014 from the NASA IRTF resolves rovibrational transitions of normal-isotope carbon dioxide as well as singly-substituted minor isotopologues, enabling remote measurements of carbon and oxygen isotope ratios as a function of latitude and local time of day. Earlier measurements obtained in October 2007 demonstrated that the relative abundance of O-18 increased linearly with increasing surface temperature over a relatively warm early-afternoon temperature range, but did not extend far enough to inspect the effect of late-afternoon cooling. These results imply that isotopically enriched gas is sequestered overnight when surface temperature is minimum and desorbs through the course of the day as temperature increases. Current spectroscopic constants indicate that the peak isotopic enrichment could be significantly greater than what has been measured *in situ*, apparently due to sampling the atmosphere at different time of day and surface temperature. The observing runs in 2012 and 2014 measured O-18 enrichment at several local times in both morning and afternoon sectors as well as at the subsolar, equatorial, and anti-subsolar latitudes. The two runs in 2014 have additionally observed O-17 and C-13 transitions in the morning sector, from local dawn to noon. These observations include a limited sampling of measurements over Gale Crater, which can be compared with contemporary *in situ* measurements by the *Curiosity* rover to investigate the degree of agreement between *in situ* and remote methods and potentially to calibrate the spectroscopic

constants required to accurately evaluate isotope ratios all over Mars.

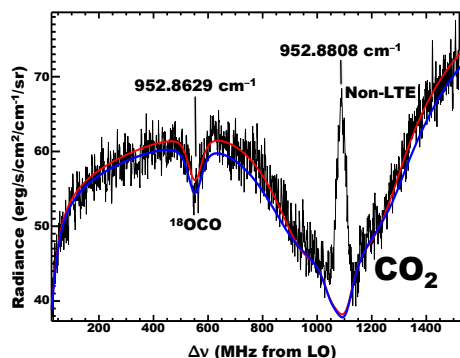


Figure 1: High-resolution infrared spectrum of CO₂ in Mars atmosphere at $952.8808 \pm 0.0534 \text{ cm}^{-1}$ (bandwidth, not uncertainty). The measured spectrum is dominated by wings of the telluric CO₂ transition at the rest frequency, spanning the Doppler-shifted CO₂ transition formed in Mars troposphere with a non-local thermodynamic equilibrium (non-LTE) core emission formed in the mesosphere, and the ¹⁸OCO absorption formed in the Mars troposphere. The blue curve models the emergent spectrum for standard temperature profile and surface temperature. The red curve arises from an iteratively improved lower-atmosphere temperature profile and surface temperature. Both models use the telluric isotope ratio, resulting in a poor fit to the ¹⁸OCO feature, demonstrating the opportunity to constrain fitting the isotope ratio.

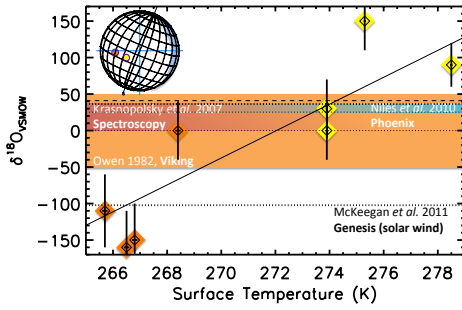


Figure 2: Spectroscopically measured deviation of Mars carbon dioxide ^{18}O from terrestrial VSMOW standard, permille (‰). Measurements on the subsolar point are orange ($\sim 0.8''$ FWHM field of view on map). Measurements at subsolar latitude, but offset 20° longitude toward planetary east (1.33 hours of local time) are in yellow. The light orange band indicates mass spectrometry by Viking landers ($0 \pm 50\text{‰}$) [4,5]; the red band indicates remote spectroscopy by Krasnopolsky *et al.* [1], $18 \pm 18\text{‰}$; and the blue band indicates *in situ* mass spectrometry from the Phoenix lander, $31.0 \pm 5.7\text{‰}$ [3]. Webster *et al.* [6] report $48 \pm 5\text{‰}$ enhancement of ^{18}O from Mars Science Laboratory, somewhat greater than Phoenix and at the upper limit of the Viking range. A dotted line indicates the unenriched solar wind measured by the Genesis mission, $-102.3 \pm 3.3\text{‰}$ [2].

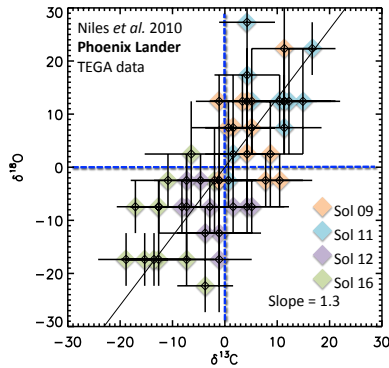


Figure 3: Corroboration from Phoenix lander measurements (data re-plotted from [3]), which show evidence for mass-dependent fractionation of isotopes, consistent with sequestration processes that significantly modify the isotopic enrichment of atmospheric CO_2 .

Acknowledgements

This research was supported by the NASA Planetary Astronomy Program. The authors were visiting astronomers at the NASA Infrared Telescope Facility, operated by the University of Hawaii under Cooperative Agreement no. NCC 5-538 with the National Aeronautics and Space Administration.

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