The Martian Carbon Cycle Probed by New Isotope Analysis

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Mars has experienced a dramatic climate change from a warm and wet environment with a large amount of water and atmosphere to its present dry and cold environment. The mystery of the loss of life and its habitable environment on Mars is important for understanding of the habitable planet environment. The isotope analysis is one of the powerful methods. NASA's Mars rover Curiosity discovered in 2022 that carbon trapped in sedimentary rocks is dramatically enriched in lighter carbon isotope (^{12}C) (House et al., 2022). This is interesting because it can be considered strong evidence for microbial life on Earth. However, the mechanism that can explain the observed carbon isotopes remain question. The comprehensive isotope analysis on the entire Martian globe at various altitude range could clarify not only the current carbon cycle on Mars but also constrain scenarios. The purpose of this study is to develop a ground-based observation method that enables global carbon isotope ratio near the Martian surface, and to clarify the carbon isotope ratio in the middle atmosphere by ESA orbiter.
Sensitive measurements of the carbon and oxygen isotope ratios in CO was achieved by the ACS and the NOMAD onboard ExoMars TGO (Alday et al., 2023; Aoki et al., 2023). Our results show a strong negative carbon isotope fractionation. However, the mechanism causing strong negative isotope fractionation still unsolved issues. We extended our analysis of NOMAD Solar Occultation observations to the 199 orbits in total from March 1st to December 24th 2022. The weighted averages of the retrieved isotope ratios at altitudes 30-50 km are δ13C = -298 ±106 ‰, δ18O = -204 ±115 ‰, and δ values of $^{13}C^{16}O/^{12}C^{18}O$ = -79 ±62 ‰, when we confine our analysis to the CO volume mixing ratios > 1500 ppm from a reliability perspective. The strong negative carbon isotope fractionation shown by our result is in good agreement with model prediction. In addition, our result indicates the obtained δ18O value is 100 ‰larger than the δ13O value. The relative differences in the isotope fractionations of carbon and oxygen are consistent with the photolysis-induced effect, as predicted by the models (Schmidt et al., 2013; Yoshida et al., 2023). We concluded that these results provide observational evidence that CO isotope fractionation is caused by CO_2 photodissociation at altitudes 30-50 km.
Remote analysis of Martian isotopes from the ground-based requires observations that are completely separate from absorption by the Earth's atmosphere. The infrared laser heterodyne spectroscopy can achieve the ultra-high spectral resolution ~10^7 in the mid-infrared regime. This capability enables observations of spectral shape sufficient to obtain the abundance of trace gases and its isotope ratio. We have developed the mid-infrared laser heterodyne spectroscopy system with the hollow optical fiber coupler, for sensitive search for isotope ratio near the surface on Mars. We demonstrated the capability of the heterodyne detection with a hollow fiber coupler for incoherent light, for the first time. We succeeded in measuring an absorption line of C_2H_4 in a gas cell with the background light source from the blackbody. The measured spectral line shape agreed well with the model. We also observed terrestrial atmospheric absorption of CO_2 with the background of sunlight. The measured intensity and spectral profile were well consistent with the model. These results demonstrated the applicability of the heterodyne spectrometer with the hollow fiber and the hollow fiber coupler to the observations of terrestrial and planetary atmospheres.
This study can be combined with the first in-situ measurement of carbon isotopes in the escaping

atmosphere from Mars by the MSA onboard MMX mission, which will be launched in 2026. The isotope fractionation could provide the strong constrain for the Martian atmospheric evolution.

Keywords: Mars, Isotope, Carbon, Spectroscopy