National Aeronautics and Space Administration

Laboratory and Modeling Constraints on the Origin of Anomalously Depleted ^{13}C on Mars

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Program: Topic

Project Objective:

- We propose to combine laboratory studies, modeling and the latest observational data to constrain the sources, transport, and sinks of organics on Mars, with emphasis on interpreting the isotopic fractionations reported by House et al.
- Two possible primary pathways for the origin of the depleted ^{13}C isotopologues of organics on Mars will be studied (Fig.1).
- The proposed work will allow us to put together a first order estimate of the carbon cycle on present and early Mars, paving the way for future work on the detailed modeling, laboratory investigations and NASA missions (e.g. MSR) to reveal the ultimate origin of organics on Mars and their implications for habitability and origin of life on paleo-Mars (Fig.2).

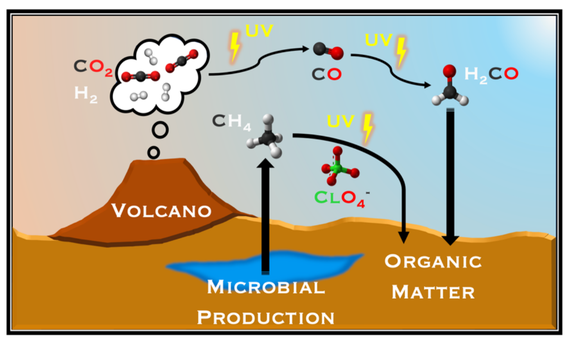

Fig. 1. Two possible scenarios for the origin of depleted ^{13}C in the carbon isotopic composition observed by SAM TLS. Deep Brown: volcanic sources of CO_2 and H_2, followed by photochemical production of H_2CO and organics. Blue: biotic sources of CH_4, followed by photochemistry and organic synthesis. Adapted from House et al.

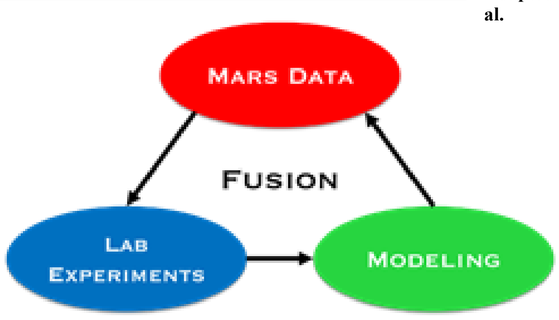

Fig. 2. Illustration of a synergetic fusion of Mars data, lab experiments and modeling to show that the organics and sulfur species together with their isotopic signatures may prove the existence of past and/or extant life on Mars.

Benefits to NASA and JPL (or significance of results):

- The preservation of ancient organic material in the regolith of Mars is a special "gift" to our Solar System. By comparison, active plate tectonics on Earth has obliterated any record of pristine material that led to the emergence of life. The Mars Exploration Program (MEPAG) advocates "Determine the habitability of an ancient environment." The Mars Sample Return (MSR) program specifically emphasizes 1. Extant or recent Martian life and 2. Biosignatures of past Martian life. *Thus, our investigation of the origin of the organics and their isotopic signature is at the heart of Mars science, as well as NASA programs such as Exobiology and Habitable World.*
- Our results could have a major influence on the choice of instrumentation and site selection in the future.

Results (Summary):

- Detected CO as the main product of CO_2 + VUV; Measured the isotopic fractionation of ^{13}CO and ^{12}CO, and determined the carbon isotope value ($\delta^{13}C$) of CO to be -125 ± 15‰.
- It was found that under current conditions of CO_2 atmosphere with H_2 mixing ratio = 10^{-5}, few organics are formed but with H_2 mixing ratio = 10^{-2}, production of organics is significantly increased.

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Results:

Experiment procedures: ***1)*** Fill the gas cell with 300-350 torr CO_2; ***2)*** Photolysis using two Hg Lamps for about 90 mins (Fig. 3); ***3)*** Photolysis product go through a LN_2 trap (to trap most CO_2) , produce about 35 mTorr of CO_2 (~25 mTorr) + CO (~10 mTorr) in about 2L volume , which then mix with roughly 700 Torr Neon; ***4)*** Deposit the gas mixture onto a CsI window at ~ 5K; ***5)*** Take FTIR absorption spectra of the matrix at 1, 0.5 and 0.25 cm^{-1} resolutions.

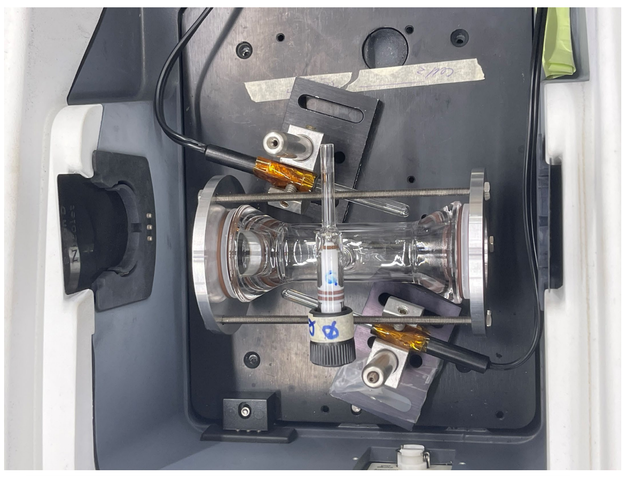


Fig. 3. Photolysis of CO_2 in a gas cell using two Hg lamps

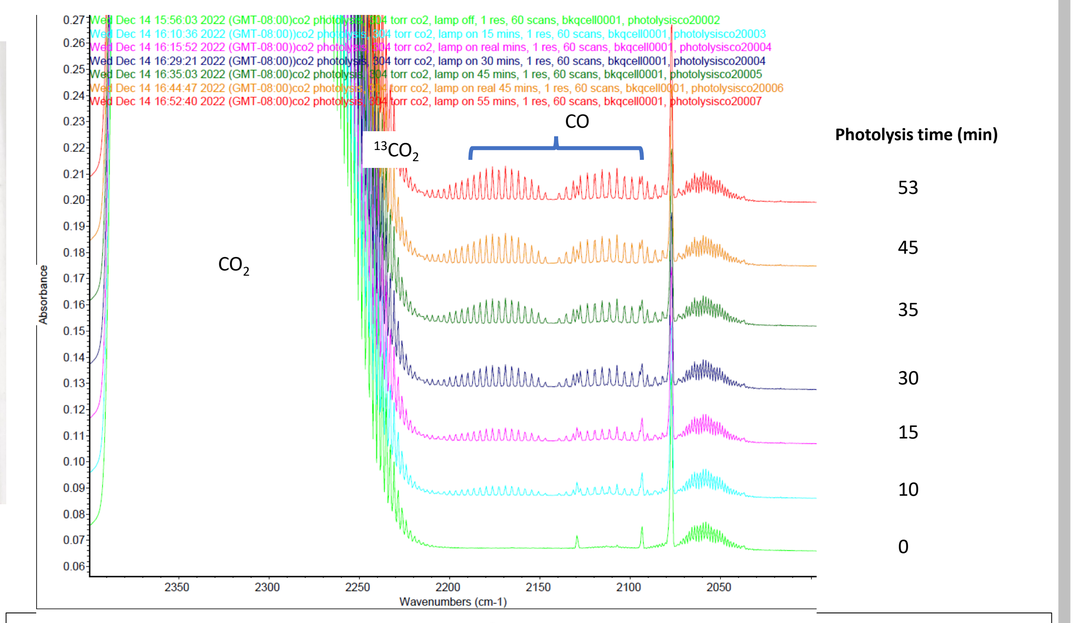
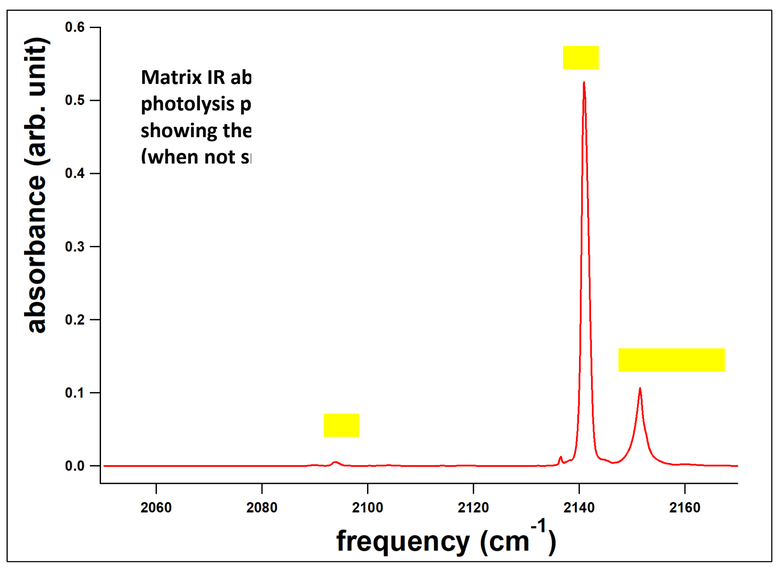
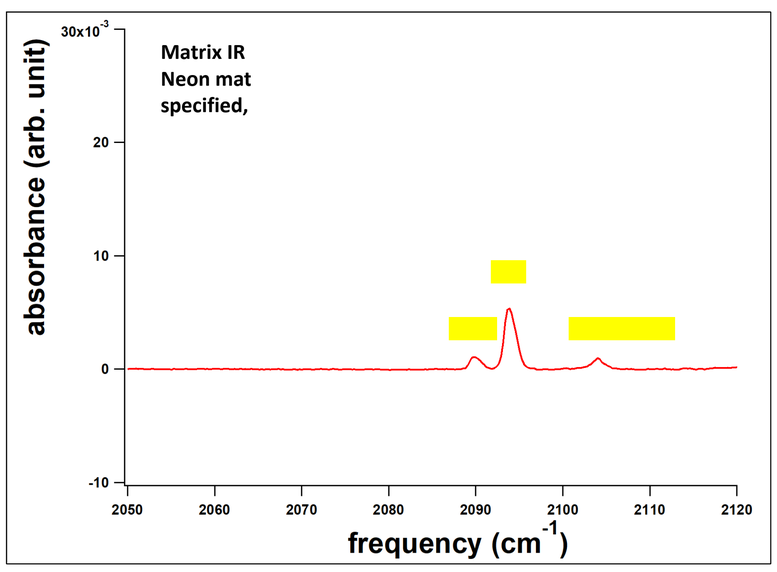
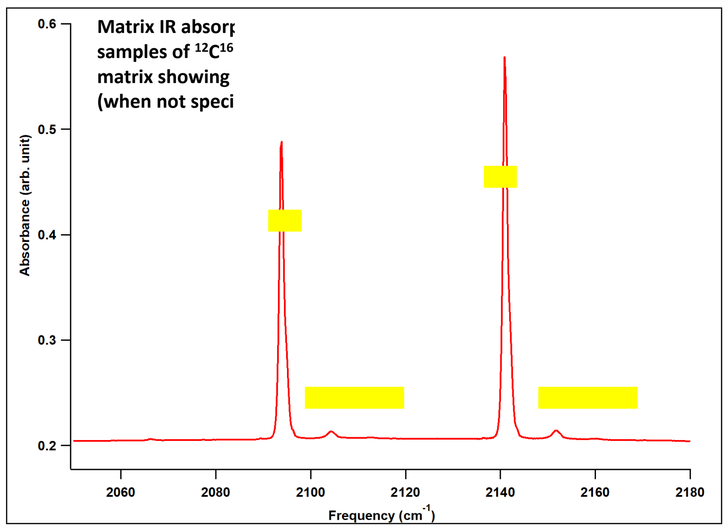


Fig. 4 IR absorption spectra of photolysis product in the gas cell CO_2 + 185 nm photons → CO







Spectral Analysis

Pee Dee Belemnite (PDB) Standard **^{13}CO: ^{12}CO ratio: 1.12372%**

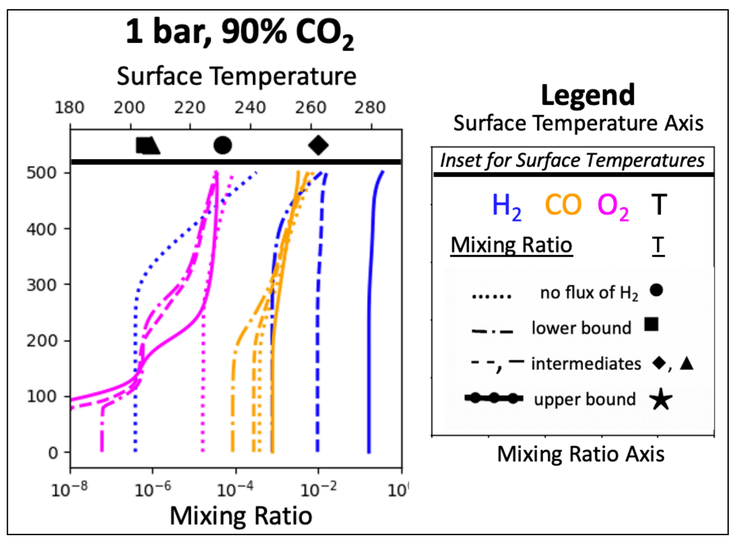
We have measured:

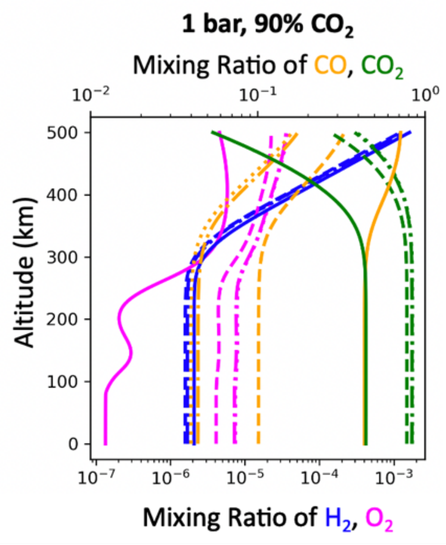
1) Original CO_2 sample: **$\delta^{13}C$ = -30.6 ‰**

2) Absorption cross section ratio (using authentic samples of $^{12}C^{16}O$ and $^{13}C^{16}O$) for **A ($^{12}C^{16}O$): A ($^{13}C^{16}O$) = 1.055**

3) After analysis of several spectra, the carbon isotope value ($\delta^{13}C$) of product CO is determined to be:

-125 ± 15‰





Mixing ratio profiles of H_2 (blue), O_2 (magenta), CO (orange), and CO_2 (green), starting with an initial 1 bar 90% CO_2 10% N_2.

The range of oxidant ground sinks include 0 (dots), 107 $cm^{-2}s^{-1}$ (dash dot), 108 $cm^{-2}s^{-1}$ (dashed), and 109 cm^{-2} s^{-1} (solid).

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