

Strong ^{13}C depletion of CO and organic synthesis in Early Mars atmosphere

Yuichiro Ueno^{1,2*}, Johan. Schmidt³, Matthew. S. Johnson³, & Shohei Aoki⁴

¹ Department of Earth and Planetary Sciences, Institute of Science Tokyo, Japan

² Earth-Life Science Institute, Tokyo, Japan

³ Department of Chemistry, University of Copenhagen, Copenhagen, Denmark.

⁴ University of Tokyo, Japan

*Presenting Author Email: ueno.y.ac@m.titech.ac.jp

Solar UV photolysis of CO_2 yields strong ^{13}C depletion of CO owing to wavelength-dependent isotope effect [1]. The inferred large carbon isotope fractionation mechanism was confirmed by our laboratory photochemical experiment [2] and is consistent with recent spectroscopic observation of Martian atmosphere [3-5]. In early Martian atmosphere, the remaining CO_2 may have enriched in ^{13}C owing to the isotope effect, even without the carbon escape into space, which is consistent with the observed C enrichment of carbonate in ALH 84001 [1,2]. Furthermore, the strongly ^{13}C -depleted CO should have been converted into aldehydes and carboxylic acids under a reducing early Mars atmosphere, and thus could have deposited into sediment [2,6]. The expected scenario could explain the observed strong ^{13}C depletion of some sedimentary organic matter in early Martian sediment [7].

References

- [1] Schmidt, J.A., Johnson, M.S., Schinke, R., 2013. Carbon dioxide photolysis from 150 to 210 nm: Singlet and triplet channel dynamics, UV-spectrum, and isotope effects. *P Natl Acad Sci USA* 110, 17691-17696.
- [2] Ueno, Y., Schmidt, J.A., Johnson, M.S., Zang, X., Gilbert, A., Kurokawa, H., Usui, T., Aoki, S., 2024. Synthesis of ^{13}C -depleted organic matter from CO in a reducing early Martian atmosphere. *Nature Geoscience* 17, 503-507.
- [3] Aoki, S., Shiobara, K., Yoshida, T., Trompet, L., Yoshida, N., Terada, N., Nakagawa, H., Liuzzi, G., Vandaele, A.C., Thomas, I.R., Villanueva, G.L., Lopez-Valverde, M.A., Brines, A., Patal, M.R., Faggi, S., Daerden, F., Erwin, J.T., Ristic, B., Bellucci, G., Lopez-Moreno, J.J., Kurokawa, H., Ueno, Y., 2023. Strong depletion of ^{13}C in CO in the atmosphere of Mars revealed by ExoMars-TGO/NOMAD. *Planetary Science Journal* 4, 97.
- [4] Alday, J., Trokhimovskiy, A., Patel, M., Fedorova, A., Lefevre, F., Montmessin, F., Holmes, J., Rajendran, K., Mason, J., Olsen, K., Belyaev, D., Korablev, O., Baggio, L., Patrakeev, A., Shakun, A., 2023. Photochemical depletion of heavy CO isotopes in the Martian atmosphere. *Nature Astronomy* 7, 867-876.
- [5] Yoshida, T., Aoki, S., Ueno, Y., Terada, N., Nakamura, Y., Shiobara, K., Yoshida, N., Nakagawa, H., Sakai, S., Koyama, S., 2023. Strong depletion of ^{13}C in CO induced by photolysis of CO_2 in the Martian atmosphere, calculated by a photochemical model. *Planetary Science Journal* 4, 53.
- [6] Koyama, S., Yoshida, T., Furukawa, Y., Terada, N., Ueno, Y., 2024b. Stable carbon isotope evolution of formaldehyde on early Mars. *Scientific Reports*. in press.
- [7] House, C.H., Wong, G.M., Webster, C.R., Flesch, G.J., Franz, H.B., Stern, J.C., Pavlov, A., Atreya, S.K., Eigenbrode, J.L., Gilbert, A., Hofmann, A.E., Millan, M., Steele, A., Glavin, D.P., Malespin, C.A., Mahaffy, P.R., 2022. Depleted carbon isotope compositions observed at Gale crater, Mars. *P Natl Acad Sci USA* 119, e2115651119.