Atmospheric origin of ^{13}C-enrichment in Martian carbonates inferred from photochemical modeling

*Shungo Koyama[1], Tatsuya Yoshida[1,2], Naoki Terada[1], Yuki Nakamura[3], Arihiro Kamada[1,2], Yoshihiro Furukawa[1], Takeshi Kuroda[1], Ryoya Sakata[3]

1. Tohoku University, 2. ELSI, Institute of Science Tokyo, 3. Research Center for Advanced Science and Technology, The University of Tokyo

Carbon is a fundamental element for life, and its cycle regulates planetary climate systems. Therefore, elucidating the carbon cycle, particularly the interactions between the atmosphere and the surface, is key to understanding planetary habitability. Mars is one of the prime candidates for investigating its potential habitability because geological evidence of past liquid water implies an active carbon cycle. Isotopic signatures provide crucial constraints for reconstructing this cycle. Recently, the Curiosity rover identified two anomalous carbon isotopic signatures in Gale Crater sediments: a strong ^{13}C-depletion in organic matter with $\delta^{13}C$ values <−100‰ (House et al., 2022) and an extreme enrichment in carbonates with $\delta^{13}C$ values of ~+100‰ (Burtt et al., 2024). While the depletion in organic matter can be explained by the deposition of photochemically produced formaldehyde resulting from CO_2 photolysis-driven fractionation (Ueno et al., 2024; Koyama et al., 2024b), the mechanism responsible for the enrichment in carbonates remains poorly constrained.

Carbonates have been identified across multiple locations on the Martian surface by both orbital remote sensing and surface rover observations (e.g., Niles et al., 2013). These carbonates are suggested to have formed in localized aqueous environments with transient water supply from the late Noachian to the present. However, the ^{13}C-enrichment of carbonates cannot be explained solely by standard equilibrium fractionation between carbonate and CO_2 in such environments (Burtt et al., 2024). This implies the existence of a heavily enriched carbon reservoir. CO_2 photolysis is a potential mechanism for such reservoir evolution. It preferentially dissociates $^{12}CO_2$, removing the light carbon as CO and leaving the remaining CO_2 enriched in ^{13}C (Schmidt et al., 2013). This mechanism may explain the observed carbon isotopic enrichment.

To test this hypothesis quantitatively, we newly implemented carbonate deposition into a coupled photochemistry-climate evolution model (Koyama et al., 2024b). Our model tracks the evolution of the carbon isotope composition of C-bearing species in the early Martian atmosphere. It comprehensively considers carbon isotope fractionation induced by CO_2 photolysis, C escape, volcanic outgassing, and the deposition of formaldehyde. The simulation starts with a weakly reducing atmosphere composed of CO, CO_2, and H_2 to account for the atmospheric evolution from reducing proto-atmospheres derived from the solar nebula and impact degassing (Yoshida and Kuramoto, 2020).

Our simulations indicate that the atmospheric redox states are closely associated with isotopic evolution. Consistent with previous results (Koyama et al., 2024b), the atmosphere transitions from a CO-dominated to a CO_2-dominated state in the late Noachian. During the CO-dominated phase, CO_2 becomes highly enriched in ^{13}C with $\delta^{13}C$ values up to ~+200‰. This extreme enrichment is driven by the high proportion of photolytic CO_2 loss relative to the total CO_2 abundance, which intensifies the fractionation effect. Notably, this isotopic evolution reproduces the signatures of ^{13}C-enrichment found in Gale Crater carbonates formed during a relatively warm climate. Furthermore, our simulations suggest that the atmosphere may have reverted to a CO-dominated state during the Hesperian and Amazonian periods,

before finally returning to a CO_2-dominated state as the atmospheric pressure approached present-day levels. In conclusion, we propose that atmospheric CO_2 photolysis serves as a unified mechanism that simultaneously explains the anomalous isotopic signatures of both ^{13}C-depleted organics and ^{13}C-enriched carbonates observed in Gale Crater. This further suggests that carbonate isotopic records serve as a proxy for early atmospheric compositions.

Keywords: Mars, Photochemistry, Stable carbon isotope, Carbonate, Organic matter, Atmosphere

