Organic matter formation from formaldehyde on Mars through time

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Introduction:

Present-day Mars is extremely cold and dry, but geomorphological and geochemical evidence indicates a warm environment compatible with surface liquid water on early Mars. In addition to water, the existence of genomic and catalytic bio-molecules that support the fundamentals of life is critical for habitability. The Sample Analysis at Mars instrument onboard the Curiosity rover discovered organic matter in the early Martian sediment [1]. Moreover, a recent analysis discovered highly variable and ^{13}C-depleted carbon isotopic values in its organic [2]. However, its origin and the availability of biologically important molecules on early Mars remain uncertain.

Formaldehyde (H_2CO), a highly soluble and reactive molecule, can be formed through photochemical reactions in planetary atmospheres. Dissolved H_2CO in water would subsequently form diverse organic matter, including bio-important molecules, such as sugars and amino acids, by the formose-type reaction [3]. Moreover, H_2CO can be generated from ^{13}C-depleted CO derived from CO_2 photolysis in the atmosphere [4]. The deposition of this photochemically produced H_2CO may explain the origin of the strong isotopic depletion observed in Martian organic matter. Therefore, investigating the atmospheric synthesis of H_2CO on early Mars is crucial for understanding prebiotic chemistry toward the potential of ancient Martian life. In this presentation, we summarize the production of H_2CO and its carbon isotope composition on Mars through time. Finally, the origin of Martian organic matter will be discussed.

Atmospheric production of formaldehyde through time: First, we investigated the global average atmospheric production and deposition of H_2CO in a 2-bar CO_2-dominated atmosphere with H_2 and CO on early Mars at ~4–3 billion years ago (Ga). We adapted a 1D photochemistry model, PROTEUS (Photochemical and RaiatiOn Transport model for Extensive USe) [5], for early Martian conditions. We utilized the temperature and H_2O vapor density profiles from the global mean results computed by a 3D Paleo-Mars Global Climate Model (PMGCM) [6] for a 2-bar CO_2-dominated atmosphere with 0, 3, and 6 % H_2 and an obliquity of 40°. Our results show that the deposition flux of H_2CO reaches the order of 10^8 or 10^9 cm^{-2} s^{-1} under conditions where the mixing ratio of H_2 is higher than 0.1%, regardless of the CO mixing ratio [7]. In a warm climate under a 6% H_2 condition, the global average deposition flux of H_2CO into the ocean is 3×10^9 cm^{-2} s^{-1}. Given the previously reported conversion rate from H_2CO to ribose [3], the calculated H_2CO deposition flux suggests a continuous supply of bio-important sugars on Noachian and early Hesperian Mars. After the warm climate periods, volcanic degassing would have decreased from the late Hesperian to the Amazonian, decreasing the mixing ratio of H_2 in the atmosphere [8]. Thus, the late Hesperian to early Amazonian was a transitional period from a high to a meager H_2CO deposition flux (Figure 1).

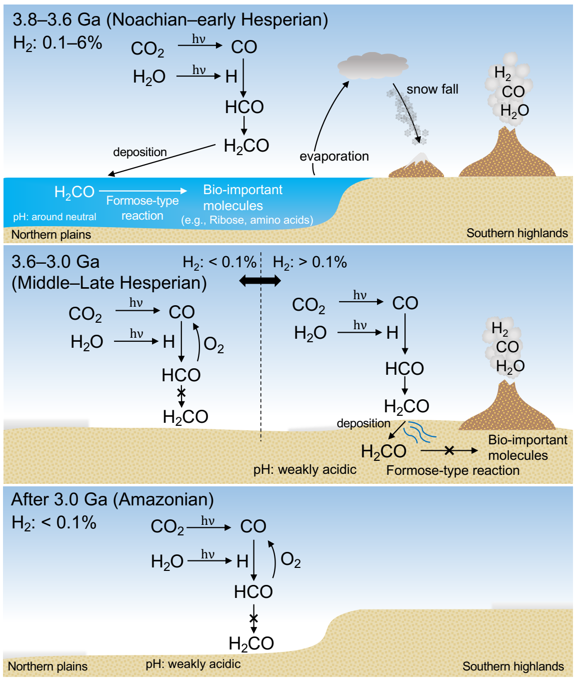

Figure 1. Scenario for the atmospheric H_2CO production on Mars through time [7].

Second, we focused on a warm climate and calculated the global distribution of H_2CO deposition across the globe in a PMGCM by creating a lookup table of H_2CO production for key atmospheric parameters: surface temperature, surface pressure, surface H_2O vapor, and UV flux. We assumed a 2-bar CO_2 atmosphere with 6% H_2 and 1% CO. As a result, the H_2CO deposition flux is higher in regions with high concentrations of H_2O vapor and efficient liquid water precipitation, corresponding to the northern ocean and its coastline at low latitudes.

Carbon isotopic ratio in H_2CO through time: Third, we developed a coupled 1D photochemistry-climate evolution model incorporating carbon isotope fractionation processes induced by CO_2 photolysis, carbon escape to space, and volcanic outgassing in an early Martian atmosphere of 0.5–2 bar, composed mainly of CO_2, CO, and H_2 to track the evolution of the carbon isotopic composition of C-bearing species [9]. The calculated carbon isotopic ratio in H_2CO shows a significant depletion in ^{13}C with a minimum ^{13}C value of approximately −200‰, resulting from the isotopic fractionation induced by CO_2 photolysis (Figure 2). This ratio varies with changes in the background atmospheric conditions, such as CO/CO_2 ratio, surface pressure, and H_2 outgassing rate. Conversely, CO_2 becomes enriched in ^{13}C, consistent with an estimate from the carbonates preserved in the Martian meteorite Allan Hills 84001. These findings imply that certain amounts of the organic matter containing strongly depleted ^{13}C in the early Martian sediment measured by the Curiosity rover could have originated from the photochemically produced H_2CO, undergoing subsequent condensation processes in water, such as formose-type reactions, during transient melting events in the late Noachian to Hesperian periods. Mixing with other organic sources, such as meteoritic material with higher δ^{13}C values, could explain the observed variable δ^{13}C values in Martian organic matter.

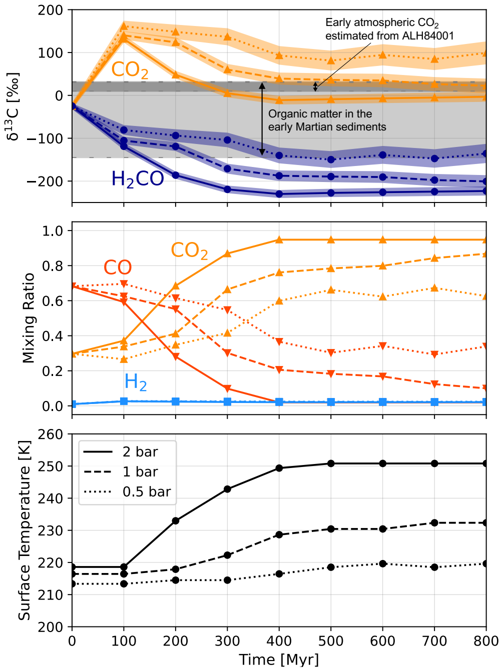

Figure 2. Evolution of δ^{13}C (upper panel) in CO_2 and H_2CO, mixing ratios of CO_2, CO, and H_2 (middle panel), and surface temperature (lower panel) for 0.5-bar (dotted line), 1-bar (dashed line), and 2-bar (solid line) atmosphere, starting from 4 Ga [9].

Conclusion: Our findings suggest that a weakly reducing early Martian atmosphere was suitable for H_2CO photochemical production, which could subsequently convert into complex organic matter, including life's building blocks, by formose reaction in water. Moreover, we showed that the carbon isotopic ratio of organic matter originating from photochemically produced H_2CO are consistent with the measurement by the Curiosity rover. These results indicate that early Mars not only retained surface liquid water but also likely hosted organic compounds such as ribose, a prebiotic precursor originating from H_2CO.

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