Large ^{13}C-depletion by solar UV CO_2 photolysis and its implication to Late Archean ecosystem

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Unusually ^{13}C-depleted organic matter are preserved in Late Archean sedimentary rocks from 2.7 to 2.5 Ga. It was hypothesized that methanotorphic bacteria efficiently incorporated ^{13}C-depleted methane into sedimentary organic carbon when photosynthesis start to provide oxygen into shallow water [1], though recent micro-scale isotopic analysis of 2.7 Ga shallow water sediment does not support the methanotorophy scenario [2]. A possible alternative cause of the ^{13}C-depletion may be input of organics produced by photochemistry in a reducing atmosphere at that time [3]. Our recent photochemistry experiment suggested that the Late Archean atmosphere would have been very reducing possibly including % level of CO or CH_4 to explain the S-MIF record including ^{36}S [4]. In such reducing atmospheres, organic matter from atmosphere may be significant for ecosystem, though its isotopic composition has not been constrained yet. Rate-limiting step of the production of organic matter in atmosphere may be photolysis of CO_2 that produces CO that is subsequently transferred into several organics including aldehyde and carboxylic acid (Kawade et al., in this volume). In this case, isotopic composition of atmospheric input would be largely controlled by fractionation of CO_2 photolysis [5]. To test the scenario, CO_2 photolysis experiment was conducted using UV source of solar-like spectrum. The results demonstrated that solar UV CO_2 photolysis causes very large C isotopic fractionation over 120‰, confirming theoretical prediction of Schmidt et al. [5]. In conclusion, highly ^{13}C-depleted organics can be derived from the reducing atmosphere that has potential to explain the negative $\delta^{13}C_{org}$ excursion from 2.7 to 2.5 Ga.

[1] Hayes (1994) *Early Life on Earth* **84**, 220-236. [2] Slotznick & Fischer (2016) *EPSL* **441**, 52-59. [3] Pavlov et al. (2000) *JGR* **105**, 11981-11990. [4] Endo et al. (2016) *EPSL* **453**, 9-22. [5] Schmidt et al. (2013) *PNAS* **110**, 17691-17696.