



Effect of Hydrocarbon Haze on Marine Primary Production in the Early Earth System

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During the Archean (4.0–2.5 Ga), atmospheric oxygen levels would have been much lower than the present value ($pO_2 < \sim 10^{-5}$ PAL) [1], and the majority of the primary production would have been carried by anoxygenic photosynthetic bacteria. In a sufficiently reducing atmosphere ($CH_4/CO_2 > \sim 0.2$) [2], the layer of hydrocarbon haze could be formed in the upper atmosphere, possibly affecting the climate. Because haze particles significantly absorb the solar UV flux, the formation of hydrocarbon haze could affect the marine microbial ecosystem via the change in the production rate of electron donors (H_2 and CO). However, how the formation of hydrocarbon haze affects the global activity of the marine microbial ecosystem remains unclear. Here, we employ a novel carbon cycle model in which a one-dimensional photochemical model “Atmos” [2], a marine microbial ecosystem model, and the carbonate-silicate geochemical cycle model are coupled. We assessed the effect of the formation of hydrocarbon haze on marine microbial ecosystems assuming completely anoxic conditions ($pO_2 < \sim 10^{-10}$ PAL) in the middle Archean and assuming mildly oxidized conditions ($pO_2 > 10^{-10}$ PAL) in the late Archean.

We found that, under the completely anoxic condition, haze formation works as a negative feedback for the oceanic biological activity. This is because the formation rate of electron donors (H_2 and CO) in the atmosphere decreases with the progress of haze formation, so that the changes in the biogenic methane flux and the haze formation rate are suppressed. More specifically, the decrease in the formation rate of electron donors is caused by the decrease in the photodissociation rate of CO_2 because of UV-shielding due to haze particles, and also by removal of C- and H-atom, which are supposed to be converted to CO and H_2 if the haze is not formed, due to rainout of haze particles.

We also found that, under the mildly oxidized condition, there are multiple equilibrium climate states that have a different haze thickness. The solution with thicker haze layer is similar to the completely anoxic condition, however, the other solution with the thinner haze layer is unique to the mildly oxidized condition. In this new equilibrium state, the formation rate of electron donors further decreases with the progress of haze formation because of the decrease in the photodissociation rate of formaldehyde. Thus, this mechanism works as a strong negative feedback for ocean biological activity and haze thickness, keeping the haze thickness thinner than the

completely anoxic condition. We show that, as a result of this negative feedback, climate with the thinner haze could be stably achieved under the mildly oxidized condition. This result is consistent with a geological record which suggests possible transient formation of the haze in the Late Archean [3]. We suggest that haze formation is a vital process in understanding the biological activity and climate stability on terrestrial Earth-like planets.

[1] Lyons et al. (2014). *Nature* 506, 307-315. [2] Arney et al. (2016). *Astrobiology* 16(11), 873-899. [3] Izon et al. (2017). *PNAS* 114(13), E2571-E2579.