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Low ^{13}C-^{13}C clumping on abiotic hydrocarbons

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Discrimination of biotic and abiotic origins of organic molecules is crucial for geochemical, environmental and astrobiological studies. Doubly-substituted isotopologues can provide insights into the biogeochemical history of a molecule, including its temperature of formation and/or its (bio)synthetic pathway [1]. We recently measured the ^{13}C-^{13}C isotopologue in ethane and ethanol by a fluorination method using a conventional isotope ratio mass spectrometer [2]. Preliminary data indicated an exceptionally low $\Delta^{13}C^{13}C$ value for putative abiotic natural gas from Kidd Creek in comparison to those measured for thermogenic ethane and biosynthetic ethanol. In order to further investigate the abiotic ^{13}C-^{13}C signature, we applied the fluorination method to ethane synthesized from methane through Gamma ray irradiation [3], spark discharge and UV photochemistry. The experimental results demonstrated that the $\Delta^{13}C^{13}C$ values of abiotic samples were systematically lower than those obtained for thermogenic ethane and biosynthetic ethanol. Putative abiotic ethane from Kidd Creek and Amadeus Basin show $\Delta^{13}C^{13}C$ values in the same range as those from abiotic experiments, with values systematically lower than thermogenic ethane by at least 0.37‰. The observed low $\Delta^{13}C^{13}C$ may possibly originate from kinetic effect associated with the polymerization step which is distinct from enzymatic or thermolytic reactions. Overall, our results show that abiotic and biotic samples can be distinguished based on the relative abundance of their ^{13}C-^{13}C isotopologue(s). Therefore, the ^{13}C-^{13}C clumping could potentially be used as a biomarker of hydrocarbon molecules, and in the long term of more complex organic molecules such as amino acids or lipids.

[1] Stolper et al. (2014) *Science* 344, 1500-1503. [2] Taguchi et al. (2020) *Rapid Commun Mass Spectrom*. 34, e8761. [3] Boreham et al. (2020), *Radiat. Phys. Chem.* 168, 108546.