

## Origin of hydrocarbons from serpentinite-hosted Hakuba Happo hot spring: Molecular and intramolecular $^{13}\text{C}$ analyses

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The early environment before the origin of Earth's life remains poorly understood due to lack of geological records during Hadean era ( $>4.0$  Ga). Serpentinite-hosted hot spring/hydrothermal systems are considered to have been widespread in Hadean Earth and a potential site to synthesize organic compounds abiotically (e.g., Russell et al., 2010). The fluid associated with low temperature ( $<100^\circ\text{C}$ ) serpentinization is characterized by strongly alkaline condition and is often rich in hydrogen ( $\text{H}_2$ ) and methane ( $\text{CH}_4$ ). Previous field studies revealed that the  $\text{C}_1$ - $\text{C}_5$  hydrocarbons were commonly observed in serpentinite-hosted systems, regardless of continental or seafloor setting [e.g., Charlou et al., 2002; Proskurowski et al., 2008; Etiope et al., 2011; Szponar et al., 2013]. However, production mechanisms of these hydrocarbons have not been poorly understood. We report chemical, and molecular and intramolecular carbon isotopic study of hydrocarbons for on-land serpentinite-hosted systems: Hakuba Happo hot spring in Japan. The spring water of the Hakuba Happo is around  $50^\circ\text{C}$  and high pH ( $\sim 10.5$ ). The main gas components were  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$ . The  $\text{CH}_4$  in Happo water has been suggested as abiogenic origin based on the previous hydrogen isotopic study (Suda et al., 2014).

The concentrations of  $\text{C}_1$  to  $\text{C}_4$  hydrocarbons were determined by Gas Chromatograph (GC) with two detectors of Pulsed Discharge Detector (PDD) and Thermal Conductivity Detector (TCD). Quantitative analysis of dissolved organic acids was performed by High Performance Liquid Chromatograph (HPLC). The  $\delta^{13}\text{C}$  values of  $\text{C}_1$  to  $\text{C}_5$  hydrocarbons were determined by using the on-line pre-concentration system coupled with the GC-C (combustion)-IRMS (isotope ratio mass spectrometer) method. For the first time, we apply a novel analytical method, namely intramolecular  $^{13}\text{C}$  analysis of propane ( $\text{C}_3\text{H}_8$ ), to a natural sample derived from the serpentinite-hosted system. The intramolecular  $^{13}\text{C}$  composition in propane was measured using the GC-pyrolysis (Py)-GC-C-IRMS system (Gilbert et al., 2016).

The isotopic trend of depletion in  $^{13}\text{C}$  with increasing molecular weight ( $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \dots$ ) was observed in Happo sample, showing similar isotopic trend compared with that of Lost City field, a seafloor serpentinite-hosted hydrothermal system (Proskurowski et al., 2008). We developed an abiotic polymerization model to account for isotopic compositions of Happo hydrocarbons. The carbon isotopic compositions of Happo hydrocarbons can be explained by the successive addition of a single carbon compound (C1-compound) with constant isotopic fractionation. The result of the intramolecular analysis revealed that the difference of  $\delta^{13}\text{C}$  values between terminal and central carbon atom positions of propane (site preference; SP in ‰) for Happo sample showed a significantly high SP value compared with that of thermogenic origin. Such a highly SP value corresponded to that expected from a polymerization model developed in this study. Thus, both molecular and intramolecular  $^{13}\text{C}$  compositions of hydrocarbons for serpentinite-hosted sample suggested that the production mechanism of these hydrocarbons was abiotic polymerization of C1-compound with a constant isotopic fractionation. The  $\delta^{13}\text{C}$  value of methane suggested that methane was a reactant C1-compound for polymerization reaction. On the other hand, the formate and acetate were detected in Hakuba Happo hot spring. Formate was the second highest concentrated dissolved C1-compound after

methane in Happo water, implying that formate was an alternative carbon source for abiotic polymerization in the serpentinite-hosted systems.

Keywords: Serpentinite, Abiogenic hydrocarbon, Intramolecular isotopic analysis, Stable carbon isotope