

Compound- and position-specific carbon isotopic study of hydrocarbons from serpentinite-hosted hot spring in Hakuba Happo, Japan

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Olivine is one of the major constituent minerals of various meteorites (Rubin, 1997). During serpentinization process of ultramafic rocks, water in contact with olivine is reduced to form molecular hydrogen (H₂) (e.g., McCollom and Bach, 2009). The highly reduced (H₂-rich) condition created by serpentinization is thermodynamically favorable for abiotic organic synthesis. Elevated concentrations of CH₄ and higher hydrocarbon gases have been 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). Abiotic synthesis has been invoked to account for the carbon isotopic distribution among low-molecular weight hydrocarbons (e.g., Proskurowski et al., 2008). However, uncertainties still remain regarding specific abiotic production mechanisms for serpentinite-hosted systems. In this study, we report a new geochemical study of hydrocarbon gases (methane, ethane, propane, butane, pentane) from the borehole well at the on-land hot spring associated with serpentinization in Hakuba Happo, Japan. We have conducted position-specific as well as compound-specific stable carbon isotopic analyses of hydrocarbons.

The gas samples were collected from Hakuba Happo hot spring that lies on an serpentinized ultramafic rock body. Highly-alkaline hot spring water with temperature of around 50°C mainly contains N₂, H₂ and CH₄ gases (Homma and Tsukahara, 2008; Suda et al., 2014). The concentrations of C₁ to C₅ hydrocarbons were determined by Gas Chromatography. A compound-specific carbon isotope measurement for C₁-C₅ hydrocarbons was performed by GC-C-IRMS coupled with an on-line pre-concentration system. A position-specific ¹³C composition in propane molecule (C₃H₈) was measured using the GC-Py-GC-C-IRMS (Gilbert et al., 2016) coupled with an on-line pre-concentration system. The straight chain alkanes (*n*-alkanes) for the Happo sample show an isotopic depletion in ¹³C with increasing carbon number ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \dots$). This ¹³C depletion trend is very similar to those of some seafloor serpentinite-hosted hydrothermal systems (Proskurowski et al., 2008; Charlou et al., 2010), and undisputed abiogenic origin for the Murchison meteorite (Yuen et al., 1984). The observed isotopic trend can be explained by a simple polymerization model developed in this study. Our model assumes that, for any particular alkane, (i) all of the subsequently added carbon atoms that are bonded to the growing carbon chain have the same isotopic composition, and (ii) those are depleted in ¹³C with respect to the first carbon atom that initiates the carbon chain. The fit of this model suggests that *n*-alkanes for the Happo sample can be formed via polymerization from single-carbon compound (potentially methane) with a constant kinetic isotopic fractionation of $-8.9 \pm 1.0\%$. To understand the type of polymerization mechanism, we next focus on the position-specific carbon isotopic compositions of hydrocarbons. For the first time, we applied a new method, namely position-specific ¹³C analysis of propane, to a natural sample derived from a serpentinite-hosted system. The difference of $\delta^{13}\text{C}$ values between terminal and central carbon atom positions of propane molecule for the Happo sample was $-1.2 \pm 0.9\%$. We show the important potential of the position-specific ¹³C analysis to identify different polymerization mechanisms that can not be discriminated by compound-specific isotopic analysis.

Keywords: serpentinite, hydrocarbon, position-specific isotope analysis, stable carbon isotope