



# Compound- and position-specific carbon isotopic signatures of abiogenic hydrocarbons from on-land serpentinite-hosted Hakuba Happo hot spring in Japan

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## Abstract

It has been proposed that serpentinite-hosted hydrothermal/hot spring systems played a significant role in the origin and early evolution of life on early Earth because abiogenic synthesis of organic compounds may accompany serpentinization. However, production mechanisms for apparently abiogenic hydrocarbons that have been observed in the ongoing serpentinizing systems are still poorly constrained. We report a new geochemical study of hydrocarbons in an on-land serpentinite-hosted hot spring in Hakuba Happo, Japan. We have conducted both compound-specific and position-specific carbon isotopic analyses of the observed C<sub>1</sub> to C<sub>5</sub> hydrocarbons. A positive linear relationship between the δ<sup>13</sup>C values and the inverse carbon number is found in C<sub>1</sub> to C<sub>5</sub> straight-chain alkanes in the Happo sample. This isotopic trend is consistent with a simple polymerization model developed in this study. Our model assumes that, for any particular alkane, all of the subsequently added carbons have the same isotopic composition, and those are depleted in <sup>13</sup>C with respect to the first carbon in the growing carbon chain. The fit of this model suggests that Happo alkanes can be produced via polymerization from methane with a constant kinetic isotopic fractionation of  $-8.9 \pm 1.0\%$ . A similar carbon isotopic relationship among alkanes has been observed in some serpentinite-hosted seafloor hydrothermal systems, indicating that the same process is responsible for the abiogenic hydrocarbon in general serpentinization fields, not only in the Hakuba Happo hot spring. Moreover, our model is also applicable to other potentially abiogenic natural gases and experimentally synthesized hydrocarbon products. For the first time, the intramolecular <sup>13</sup>C composition of propane from a natural sample derived from a serpentinite-hosted system was determined. The intramolecular <sup>13</sup>C distribution in propane shows the important potential to identify different polymerization mechanisms that cannot be discriminated by compound-specific isotopic analysis.

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## 1. INTRODUCTION

Serpentinite-hosted systems are considered to be important sites for the abiotic synthesis of organic compounds, which may have been a crucial stage in the origin of life on Earth (e.g., Russell et al., 2010). The fluid associated with serpentinization is generally characterized by high concentrations of hydrogen ( $H_2$ ) and methane ( $CH_4$ ) (e.g., Neal and Stanger, 1983; Abrajano et al., 1988; Charlou et al., 1998, 2002, 2010; Kelley et al., 2001; Etiope et al., 2011; Morrill et al., 2013; Szponar et al., 2013; Suda et al., 2014a; Yuce et al., 2014; McDermott et al., 2015). Moreover, previous field studies have revealed the presence of non-methane hydrocarbons (NMHCs) in serpentinite-hosted systems, regardless of a continental or seafloor setting; seafloor: Rainbow, Logatchev, Ashadoze (Charlou et al., 2002, 2010), Lost City (Proskurowski et al., 2008), Von Damm (McDermott et al., 2015), on-land: Chimaera (Etiope et al., 2011), Genova (Boschetti et al., 2013), Cedars (Morrill et al., 2013), Tablelands (Szponar et al., 2013), Tahtakopru (Yuce et al., 2014). A carbon isotopic trend showing  $^{13}C$  depletion of higher hydrocarbons ( $C_2$  to  $C_5$ ) with respect to methane ( $C_1$ ) has been suggested to be an indicator of abiogenesis, at least for some serpentinite-hosted systems (Proskurowski et al., 2008; Charlou et al., 2010; Etiope et al., 2011; Szponar et al., 2013). However, uncertainties still remain regarding specific abiotic production mechanisms and their associated isotope fractionation factors for serpentinite-hosted systems.

Compound-specific carbon isotopic analysis of individual hydrocarbons (methane, ethane, propane, butane, pentane) have commonly been used in order to understand the origins and histories of natural hydrocarbons in geochemical settings. On the other hand, position-specific isotope analyses (PSIA), also referred to as intramolecular isotopic analyses, have mainly been applied to metabolic studies using biological samples: amino acids (Abelson and Hoering, 1961), acetic acid (Meinschein et al., 1974), vanillin (Krueger and Krueger, 1983), acetoin (Rinaldi et al., 1974), glucose (Rossmann et al., 1991). In principle, information on the origins and histories of organic molecules should be recorded in specific positions of the molecule, including abiotic hydrocarbons from hydrothermal systems. While PSIA has been shown to be a useful tool to constrain the origin and/or the biosynthetic pathway of naturally occurring molecules, the requirement of a large sample size for PSIA makes applications limited to natural organic molecules that are present in high concentrations. Recently, Gilbert et al. developed a novel method for analyzing the intramolecular  $^{13}C$  composition of propane and, for the first time, reported the difference of  $\delta^{13}C$  values between terminal and central carbon atom positions of propane (Gilbert et al., 2016). They successfully measured the intramolecular  $^{13}C$  distribution of a natural gas sample of thermogenic origin ( $C_3H_8 = 1.3$  vol.%), and demonstrated that intramolecular carbon isotope distributions obtained from a thermogenic natural propane sample were consistent with that expected from theoretical models of thermal cracking (Gilbert et al., 2016).

Here, we report new data for hydrocarbon gases (methane, ethane, propane, *iso*-butane, *n*-butane, *iso*-pentane, and *n*-pentane) and organic acids from the borehole well at the on-land hot spring associated with serpentinization in Hakuba Happo, Japan. A previous study based on the hydrogen isotopes suggested that methane in Happo #1, one of the two wells in Hakuba-Happo, was abiogenic (Suda et al., 2014a,b). In order to investigate the  $C_{2+}$  hydrocarbons production mechanism, we propose a model accounting for the observed compound-specific compositions of  $C_1$ – $C_5$  hydrocarbons formed through the abiotic polymerization process. In addition, position-specific isotope analysis of propane is applied to the Hakuba Happo sample by improving the previous method of Gilbert et al. (2016). We thus discuss the production mechanism of hydrocarbons utilizing the combination of compound-specific and position-specific carbon isotopic compositions.

## 2. GEOLOGICAL SETTING

Hakuba Happo hot spring (36°42'N, 137°48'E) is located in the Shiroumadake area, which belongs to the Hida Marginal Tectonic Belt lying to the west of the Itoigawa–Shizuoka Tectonic Line (ISTL) in central Japan. In Shiroumadake area, the serpentinized ultramafic rocks form two wide zones, referred to as “Renge serpentinite (abbrev., ‘sp.’) zone” and “Happo sp. zone” in this study (Fig. 1a). The zones are largely covered by Lower Jurassic sedimentary rocks and younger volcanics and sedimentary rocks (e.g., Nakano et al., 2002). The ultramafic rocks are mostly serpentinized and sheared, or thermally metamorphosed by the Mesozoic to Cenozoic intrusive rocks (Nakamizu et al., 1989; Nakano et al., 2002). On the other hand, relatively fresh olivine remains in the Happo sp. zone (Nakamizu et al., 1989; Nakano et al., 2002). Active hot springs are distributed sporadically along the ISTL owing to recent volcanic activity (Homma and Tsukahara, 2008). Hakuba Happo hot spring lies on an ultramafic rock body in the Happo sp. zone (Fig. 1b). The hyper-alkaline waters (pH > 10.6), with temperatures of approximately 50 °C, are pumped from two borehole wells (Happo #1 and Happo #3). Hakuba Happo waters contain high concentrations of  $H_2$  and  $CH_4$  (Suda et al., 2014a). The  $CH_4$  from Happo #1 well has been suggested to be mainly of abiogenic origin based on a previous study (Suda et al., 2014a, 2014b).

## 3. METHODS

### 3.1. Sample collection and in-situ measurements

Our investigation of Happo #1 well has been conducted during the period from June 2011 to June 2015. Water temperature, pH, dissolved oxygen level (DO), electrical conductivity (EC), salinity (SAL), and oxidation–reduction potential (ORP) were measured using portable sensors in the field at the time of collection. Hakuba Happo hot spring water was pumped from the boreholes and then flowed out through a hose. During the collection of water and gas sam-

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