Radiocarbon and noble gas isotope study to constrain origin of methane in Hakuba Happo serpentinite-hosted hot spring

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Serpentinite-hosted systems attract more interest from the perspective of studying the origin of life. High concentrations of methane (CH_4) and higher hydrocarbons (C_{2+}) are commonly observed in serpentinite-hosted systems (e.g., Schrenk et al., 2013; Etiope and Sherwood-Lollar, 2013). Previous studies have suggested that stable hydrogen and carbon isotopic compositions of hydrocarbons are compatible with abiotic formation via polymerization process (Proskurowski et al., 2008; Suda et al., 2017). However, little is known about when and where the hydrocarbon synthesis occurs. Our purpose is to constrain both the time and place for methane production by analyzing radiocarbon isotope (^{14}C) and noble gas isotopes (^{3}He, ^{4}He, ^{20}Ne) in the serpentinite-hosted hot spring in Hakuba Happo, Japan. Hakuba Happo hot spring lies on a serpentinized ultramafic rock body in the Shiroumadake area, which belongs to the Hida Marginal Tectonic Belt in central Japan. Hyperalkaline hot spring water (ca. 50˚C, pH = 10.6) rich in H_2 and CH_4 gas is pumped from two borehole wells; Happo #1 and Happo #3 (Homma and Tsukahara, 2008; Suda et al., 2014). Sample collection was conducted between 2015 and 2018. In the same manner as Suda et al. (2017), gas and water samples were obtained from two borehole wells. Pipe-scale carbonate samples of the Happo #1 borehole well were collected at the timing of when the old water-pumping pipes were replaced with new pipes in 2016. For the ^{14}C measurements of CH_4, a sample preparation step of CH_4 combustion to CO_2 was conducted at JAMSTEC by using the custom-built flow-through vacuum line system, which was based on Pack et al. (2015). Radiocarbon contents of purified CO_2 samples were determined at the University of Tokyo by using the graphitization system (Yokoyama et al., 2007) and the Accelerator Mass Spectrometry (AMS). The sample preparation and ^{14}C-AMS measurement for carbonate samples were conducted at the University of Tokyo by using an automated sample preparation system, which is composed of an elemental analyzer and a glass vacuum line based on Kato et al. (2014). Noble gas isotope abundances were measured with a noble gas mass spectrometer at GSJ, AIST. The concentration of dissolved inorganic carbon (DIC) in spring water was measured by using GasBench/IRMS system at GSJ, AIST.

We found that ^{14}C contents in CH_4 were close to the detectable limit, whereas pipe-scale carbonates which precipitated from hot spring water contained the detectable ^{14}C. Radiocarbon evidence rules out a modern carbon (e.g., atmospheric CO_2, organics in surface soil) as the carbon source for CH_4, suggesting that Hakuba Happo CH_4 is derived from old carbon source in deep crust or mantle. In Hakuba Happo hot spring, CO and CO_2 were below detection limit (<0.0005 vol.%). DIC concentration was <28 μmol/L (upper values because of suspicion of air contamination during sampling), which was lower than dissolved CH_4 concentration (124-664 μmol/L; Suda et al., 2014). If CH_4 production occurs under on-site condition, the inorganic carbon compounds (CO, CO_2 and DIC) are not likely to be a carbon source for CH_4. The high helium isotope ratio ($^{3}He/^{4}He$) was observed in both well sites, indicating that a major portion of He is mantle derived. In Shiroumadake area, the $^{3}He/^{4}He$ ratios tend to decrease with distance from Norikura Volcanic Chain, suggesting volcanic gases are dissolved in groundwater and then brought to surrounding hot spring. The $CH_4/^{3}He$ ratios of Hakuba Happo samples were one order of magnitude higher than those of other hot springs which are not directly related to serpentinite rocks. Exceptionally

high $CH_4/^3He$ ratio can not be explained by simple influx of mantle-derived CH_4. Another CH_4 source different from mantle-CH_4 may be required. Based on the ^{14}C and noble gas results, we suggest that a major portion of CH_4 at Hakuba Happo is produced in deep crust rather than shallow and modern groundwater.

Keywords: Serprntinite, hyperalkaline hot spring, methane, radiocarbon, noble gas isotope

