Constraint on the origin of methane from Hakuba Happo serpentinite-hosted hot spring by using $^{14}CH_4$ and noble gas isotope

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Ultramafic rock-water interaction systems attract more interest from the perspective of study for origin of life since the discovery of the hyperalkaline hydrothermal system in the Atlantic Ocean in 2001 (Kelley et al., 2001). These serpentinite-hosted systems are generally characterized by high concentrations of methane (CH_4) and higher hydrocarbons (C^{2+}) regardless of seafloor or on-land (e.g., Schrenk et al., 2013; Etiope and Sherwood-Lollar, 2013). Previous stable carbon and hydrogen isotopic studies have suggested that hydrocarbons could be formed abiotically via polymerization process (Proskurowski et al., 2008; Suda et al., 2017). However, the following is still poorly constrained; when and where hydrocarbons are produced. In this study, to constrain the origin of methane, we determined the radiocarbon (^{14}C) content in CH_4 and the helium isotope obtained from serpentinite-hosted hot spring in Hakuba Happo.
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. The hyperalkaline waters (pH>10), with temperatures of approximately 50°C, are pumped from two borehole wells (Happo #1 and Happo #3). N_2, H_2 and CH_4 are main gas components (Homma and Tsukahara, 2008; Suda et al., 2014). Water chemistry and volatile component are controlled primarily by serpentinization reaction.
Sample collection was conducted in 2015-2018. Hot spring gas samples were collected by a displacement method in water from two borehole wells (Happo #1 and Happo #3). For radiocarbon (^{14}C) analysis of methane, firstly, CH_4 in gas samples was converted to CO_2 by using the custom-built flow-through vacuum line system (similar to Pack et al., 2015) at JAMSTEC. Secondly, the purified CO_2 gas was reduced to graphite by using the graphitization reactor with Fe powder and hydrogen gas, and then the ^{14}C content was determined by using an accelerator mass spectrometry (AMS) at AORI, the University of Tokyo. Noble gas isotope abundances were measured with a noble gas mass spectrometer at GSJ, AIST. The concentrations of CO and CO_2 in gas phase were determined by using a GC-methanizer-FID method, which was suitable for detection of trace amounts of CO and CO_2 (Kaminski et al., 2003). The concentration of dissolved inorganic carbon (DIC) in spring water was measured by using GasBench/IRMS system at GSJ, AIST.
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 methane concentration (124-664 μmol/L; Suda et al., 2014). Methane is the most abundant carbon compound in Hakuba Happo hot spring. If methane 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 ($^3He/^4He$) was observed in both well sites. The $^3He/^4He$ ratios for Happo #1 and Happo #3 were 4.10 R_{atm} and 4.47 R_{atm}, respectively (where R_{atm} is the atmospheric $^3He/^4He$ ratio of 1.4×10^{-6}). For Happo #1 site, relative contribution of air, mantle and crustal components are estimated to be 47%, 31% and 22%, respectively. For Happo #3 site, 69%, 24% and 8%, respectively. The result of AMS measurements on two CH_4 samples from Hakuba Happo reveals that ^{14}C contents are near the detectable limit, i.e., the ^{14}C ages of CH_4 is at least approximately 50,000 years before present. Radiocarbon evidence rules out a modern carbon compound (e.g., atmospheric CO_2, organics in surface

soil) as the carbon source of CH_4 at Hakuba Happo hot spring system. The helium isotope and $^{14}CH_4$ data could be consistent with deep-derived carbon source of the Hakuba Happo CH_4. Therefore, it will be important to consider a relation between surface reaction system and deep mantle/crustal system.

Keywords: serpentinite, hyperalkaline hot spring, methane, radiocarbon, helium isotope