

Sourcing methane from Tablelands, Gros Morne National Park, Newfoundland, Canada, and comparing extraction methods for dissolved gas sampling

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The Tablelands massif in Western NL is a terrestrial site of serpentinization that possesses characteristics that are conducive to all three established pathways of methanogenesis – abiogenic, microbial, and thermogenic - or a combination thereof. Methanogenic characterization is traditionally accomplished by analyzing the stable isotope composition of the produced methane (the $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$) in conjunction with geologic, geochemical, and microbiological and genomic evidence. An ultra-basic, reducing spring (WHC2b) within the massif has been studied extensively. Previous geochemical characterization of WHC2b has included the $\delta^{13}\text{C}_{\text{CH}_4}$ but this study constitutes the first analysis of $\delta^2\text{H}_{\text{CH}_4}$ for the Tablelands. Additionally, two field sampling techniques for the collection of methane for isotopic analysis; vacuum extraction and gas stripping, were tested in the laboratory and then deployed in the field to determine if each method maintained the methane's isotopic ratios and to determine their relative suitability for methane provenance studies. The $\delta^{13}\text{C}_{\text{CH}_4}$ value of methane collected in 2016 via vacuum extraction was $-27.6 \pm 0.3\text{‰}$, while the $\delta^{13}\text{C}_{\text{CH}_4}$ value of methane collected via gas stripping in 2016 was $-27.7 \pm 0.0\text{‰}$. Carbon isotope values of methane were consistent, between differing sampling methods. The $\delta^2\text{H}_{\text{CH}_4}$ values of methane collected via vacuum extraction and gas stripping, analyzed in 2016, were $-181\text{‰} \pm 4$ and $-181\text{‰} \pm 2$, respectively. Hydrogen isotope values of methane were consistent between sampling methods. The stable carbon isotope composition of methane in WHC2b was consistent over an eight-year span according to data collated from five individual studies of the spring, with a $\delta^{13}\text{C}_{\text{CH}_4}$ value of methane of $-27.1 \pm 0.5\text{‰}$ ($n = 5$), making isotope systematics a tool for discriminating between methane sources. Geochemical, microbiological, and statistical means of discriminating between methanogenic pathways were applied to WHC2b, and methane was characterized as non-microbial.