Clumped isotopologue constraints on the origin of methane in basalt- and ultramafic-hosted mid-ocean ridge hydrothermal fluids

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Hot spring fluids emanating from unsedimented mid-ocean ridge hydrothermal systems hosted in basalt and ultramafic rock commonly contain high concentrations of methane. Multiple hypotheses have been proposed for the origin(s) of this methane, ranging from synthesis via aqueous reduction of inorganic carbon (ΣCO_2) [1] to leaching of methane-rich fluid inclusions formed in minerals such as olivine at depth [2–3]. To place constraints on the mechanism(s) reponsible for methane generation in these systems, we determined the relative abundance of four stable isotopologues of methane ($^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$, a "clumped" isotopologue) in geochemically diverse fluids of varying temperatures sampled at the Rainbow, Von Damm, Lost City, and Lucky Strike hydrothermal vent fields.

The data indicate highly uniform clumped isotopologue temperatures (averaging $310^{+53}/_{-42}$ °C) across the suite of fluids, with no apparent relation to the wide range of geologic settings, fluid temperatures (96 to 370 °C) and chemical compositions (pH, $[H_2]$, $[\Sigma CO_2]$, $[CH_4]$) represented. Combined with stable isotope ratio data ($^{13}C/^{12}C$ and D/H of methane), the available constraints suggest a common mechanism of methane generation at depth, the most likely of which is leaching of volatile-rich fluid inclusions. Apparent isotopologue equilibrium at temperatures of ca. 270 to 360 °C is consistent with thermodynamically favorable reduction of $CO_2(g)$ to $CH_4(g)$ with $H_2(g)$ in inclusions at temperatures below ca. 400 °C under redox conditions that characterize submarine hot spring systems.

[1] Proskurowski et al. (2008) *Science* **319**, 604–607; [2] Kelley (1996) *JGR* **101**, 2943–2962; [3] McDermott et al. (2015) *PNAS* **112**, 7668–7672.