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Clumped methane isotopologues reveal hidden processes in the submarine crustal biosphere

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The upper (40-500 m) oceanic basaltic crust holds cold to warm seawater-derived hydrothermal fluids, hosting a microbial deep biosphere. On the eastern flank of Juan de Fuca Ridge (JdFR), the 3.5 Myr old basaltic crust is covered by thick (~250 m) sediment that allows the basement fluid to geothermally warm to a moderate temperature of ~65°C. The anoxic warm fluid, containing negligible to undetectable nitrate, is rich in sulfate (18 mM) but poor in dissolved organic carbon (12 μM) and carries a significant amount of methane (1.5-76 mM) that varies among sampling sites, depths and times (Lin et al., 2014). In 2023, we revisited the sub-basement environment along the Juan de Fuca Ridge flank, aiming to use isotopologues of CH_4 ($^{13}CH_3D$ and $^{12}CH_2D_2$) to distinguish sources from processes of the methane in this aquifer.

Deeply buried basaltic-hosted fluids were pumped into foil-lined bags via fluid delivery lines associated with Integrated Ocean Drilling Program (IODP) Circulation Obviation Retrofit Kits (CORKs) that extend from basement depths to the outlet ports at the seafloor. By overcoming sampling, methane purification, and analytical challenges, we obtained the first clumped isotopologue measurements for dissolved methane in the submarine basaltic aquifer at the JdFR flank, in which the hydrothermal fluid carried methane ranging from 0.5 to 63 μM. One sample identified as abiotic on the traditional Schoell diagram (bulk $\delta^{13}C$ versus $\delta^{2}H$) was not on the abiotic region of the $\Delta^{13}CH_3D$ versus $\Delta^{12}CH_2D_2$ diagram. Rather, this sample had a very high $\Delta^{12}CH_2D_2$ value, suggesting that the methane from this sampling site had gone through other processes rather than simply reflecting its origin (abiotic or biotic). Future research will evaluate which isotope fractionation mechanisms or dramatic mixing could support the clumped methane isotope observations of the Juan de Fuca Ridge crustal fluids, revealing the cryptic methane cycle in this deep subsurface aquifer.

Ref: Lin et al. (2014) Dissolved hydrogen and methane in the oceanic basaltic biosphere. EPSL. 405, 62-73.