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The unique signature of DOC found at 9.5˚N East Pacific Rise hydrothermal vent site: A hotbed for condensed aromatic and sulfur-containing formulas

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Deep ocean dissolved organic matter (DOM) has long been suspected to be influenced by hydrothermal processes, with indirect evidence from background oceanic samples suggesting hydrothermal vent derived contributions. Yet hydrothermal vents remain an understudied source of DOM, largely due to the volumes and equipment required to sample these environments. Here, we present a detailed molecular characterization of DOM collected directly from six active hydrothermal vents and associated plumes at the 9.5˚N East Pacific Rise. We hypothesize that hydrothermal vent DOM is compositionally distinct from background deep ocean DOM, and that distinct characteristics will be observed between hot and diffuse flows and their respective plumes. Samples were filtered to 0.3 μm and extracted via PPL solid-phase cartridges. FT-ICR-MS (21T) analysis in both ESI+ and ESI− ionization modes was combined with ^{1}H NMR measurements to provide complementary structural information across the DOM pool. We find that vent DOM is distinct from background deep ocean DOM, containing a high abundance of condensed aromatic and sulfur bearing molecular formulas unique to the vent system samples. An apparent mixing of vent fluid was observed between vent and plume sample pairs. NMR analysis revealed distinct chemical shifts between functional groups present, with hotter vents dominated by aliphatic and aromatic groups, which appear to be controlled by vent temperature. Differences between vent and plume types will be assessed, as will comparisons between pre- and post-hydrothermal eruption. These findings demonstrate that hydrothermal vents are a significant source of condensed aromatic DOC to the deep ocean reservoir, contributing to the anomalously aged DOC.