Supplementary materials for the G3 manuscript 2020GC009481

Title: Organic Biogeochemistry in West Mata, NE Lau Hydrothermal Vent Fields

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Table of contents

Main text- Extremely high dissolved organic carbon in Epsilon: abiogenic production?

Fig S1. Energetics of the formic acid synthesis.

Table S1. Log equilibrium constants (K) for formic acid (HCOOH) production.

Table S2. Reported or estimated chemical compositions of Epsilon hydrothermal vent.

Extremely high dissolved organic carbon in Epsilon: abiogenic production?

The very high DOC concentration of the Epsilon fluids (521 μM, Table 2 in main text) measured in acidic fluids emanating from Epsilon is surprising. The high DOC concentrations cause for skepticism and inquiry into the possibility of contamination or sampling artifacts. The highest DOC values occur in samples with low pH, so we investigated the possibility of carbon leaching from sampler and sample storage bottles. The highest DOC blank (1N H_2SO_4 leached for 20 hours) had a concentration of only 1-2% of the high values measured. We cannot duplicate the rapidly changing temperature and pressure conditions of seafloor sampling in the lab, but the blank testing indicates that leaching DOC from the samplers and sample bottles cannot account for high measured DOC concentration. In addition, although there is only one sample, this sample is also high in Si and Fe. Both high Si and high Fe in hydrothermal fluids are indicators of high-temperature water-rock reactions (Von Damm, 1990; Butterfield et al., 1997; Von Damm et al., 2006).

Discharging fluids might have entrained high DOC fluids from a productive subseafloor microbial habitat. For example, thermophiles isolated from event plumes associated with the 1996 eruption at North Gorda Ridge implied that these thermophiles—present before the North Gorda Ridge eruption event—were expelled from members of a native subseafloor community during the extremely high flux of water and heat from the ocean crust (Summit and Baross, 1998). Similar to the discharge of microorganisms during an eruptive event, the observed high DOC could have been entrained from a productive deep subseafloor microbial community in the volume surrounding the conduit connecting the seafloor vent to a sub-seafloor magma chamber (Fig. 4 of the main text). The discharged fluids (~30°C) were not heated enough to sufficiently oxidize DOC completely into CO_2, allowing high concentrations of DOC values to remains in the fluids collected.

In addition to biotic DOC, abiogenic organic carbon may be another source for the high DOC. There is a thermodynamic drive for the formation of metastable organic species such as formic/formate acid in submarine hydrothermal vents. Based on elevated concentrations and unique isotopic compositions, abiogenic formate up to 144 μM and 669 μM, respectively, have been suggested to be produced from reduction of inorganic carbon by high concentrations of dissolved H_2 in serpentine-hosted vent fields at Lost City (up to 15 mM; Lang et al., 2010) and Von Damm (up to 18.2 mM; McDermott et al., 2015). Formate production under submarine hydrothermal conditions at Von Damm vent field is also supported by results of thermodynamic modeling (Shock, 1992; McDermott et al., 2015).

To investigate whether the chemical and physical condition of the fluid flowing out at Epsilon may also favor abiogenic production of formic acid, the dominate formate species at pH ~2 (Seewald et al., 2006), thermodynamic modeling is performed for the CO_2 reduction reaction below:

$$CO_{2(aq)} + H_{2(aq)} \rightarrow HCOOH_{(aq)} \qquad (1)$$

Details of the method and parameters used for the modeling are provided in the supplementary materials (Table S1 & S2). The model evaluated the energetics for an aquatic environment with formic acid of 10 µM and of 521 µM. The former is to represent a low formic acid concentration that is at least an order of magnitude higher than the formic acid concentrations in deep seawater, which is often under the detection limit of 1 µM (Lang et al., 2010). The latter is to represent the highest measured DOC in our collected sample from Epsilon (Table 2 in main text).

While the reaction temperature is not known, we calculated the energetics of reaction over temperatures ranged from 4°C and 300°C. The pressure is set at 120 bar (i.e. water depth of ~1215m). The activity coefficients of neutral species, formic acid, H_2 and CO_2 can be assumed to be unity (Seewald et al., 2006; McDermott et al., 2015). Although Epsilon is located close to the eruptive sites, the measured dissolved hydrogen concentration was 0.058 mmol/Kg (Baumberger et al., 2014), only slightly higher than that in Luo (0.0013 mmol/Kg) or in Kohu (0.013 mmo/Kg) (Baumberger et al., 2014). Spontaneous reaction for abiotic formic acid production does not precede (Fig. S1). Therefore, the high DOC at Epsilon cannot be explained by abiotic formic acid production.

Over a reaction temperature between 4°C and 300°C, abiogenic production of low concentrations of formic acid (i.e. 10 µM) becomes thermodynamically plausible in a postulated hydrothermal fluid with high concentrations of H_2 (30 mmol/Kg) and CO_2 (80 mmol/Kg) (Fig. S1, Table S2). With such high H_2 and CO_2, the reduction of CO_2 to form formic acid concentration up to 521 µM remains spontaneous at a reaction temperature between (4°C) and up to ~180°C. s

While hydrocarbons may also form via catalytic Fischer-Tropsch type (FTT) synthesis reactions under hydrothermal conditions and have been synthesized in laboratory-controlled experiments (Foustoukos and Seyfried, 2004; McCollom and Seewald, 2006; McCollom and Seewald, 2007), kinetic barriers preclude the formation of CH_4 in the C-H-O chemical system (Shock, 1990; Shock, 1992; McDermott et al., 2015) and thus we do not consider the abiotic formation of CH_4 in this work. For details on the compositions of dissolved gases, we encourage the readers to the work by Baumberger et al. (2014).

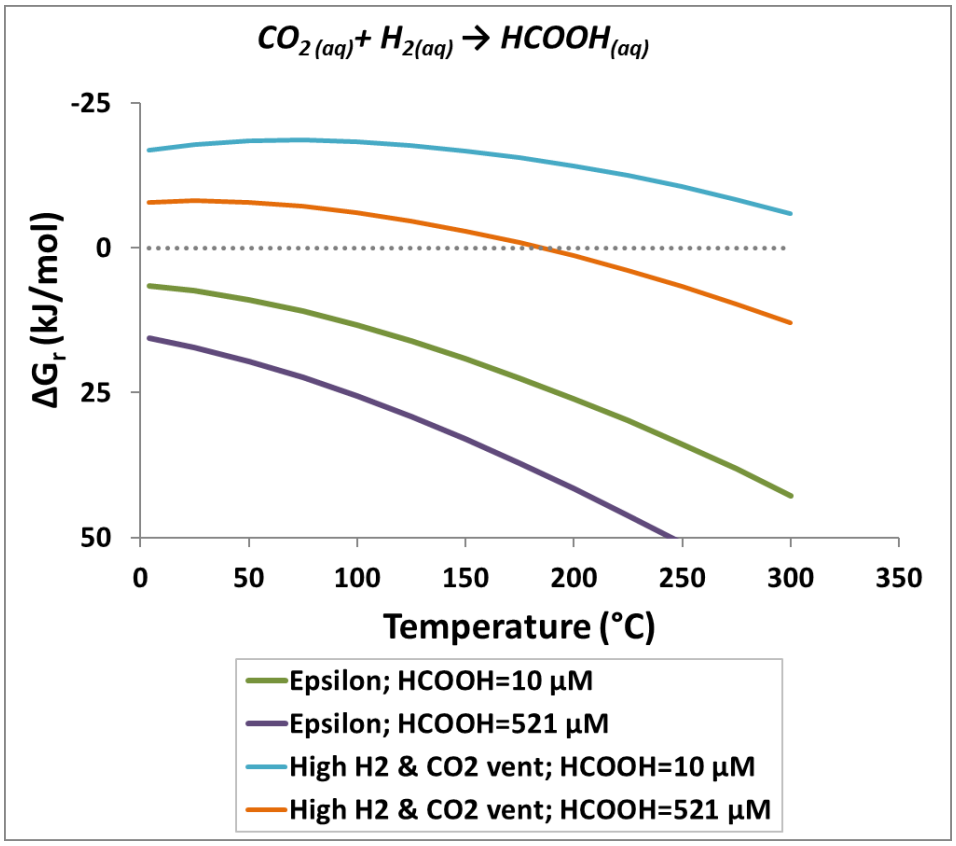

Fig S1. Energetics of the formic acid synthesis reactions listed in the figure title at 110 bar and temperatures ranged from 4°C and 300°C. The activities of H_2(aq), $CO_{2(aq)}$, bicarbonate and pH used in the calculation are taken from Table S1 and S2. Negative values of ΔGr indicate that the reactions as written in the figure, and under the specified conditions, are favored to progress to the right.

Table S1. Log equilibrium constants (K) for formic acid (HCOOH) produced from dissolved carbon dioxide (CO_2) and hydrogen (H_2) at 120 bar and at various temperatures.

Temperature (°C)	LOG K
4	0.817
25	0.759
50	0.608
75	0.410
100	0.185
125	-0.056
150	-0.306
175	-0.561
200	-0.817
225	-1.074
250	-1.330
275	-1.586
300	-1.842

Table S2. Reported or estimated chemical compositions of the Epsilon hydrothermal vent at W. Mata used for thermodynamic modeling.

Chemical species	Unit	Event plume	Epsilon	Postulated high H_2 & CO_2 vent
$[H_2]$[a]	mol/kg	0.000015	0.000058	0.03
$[CO_2]$[b]	mol/kg	0.00038	0.00151	0.08
log $\{H_2\}$		-4.8	-4.2	-1.5
log$\{CO_2\}$		-3.4	-2.8	-1.1

a. Baumberger et al. (2014)
b. The CO_2 concentrations for Epsilon were estimated by multiplying the H_2 from Baumberger et al. (2014) to the $\triangle CO_2$: H_2 ratio =14566nM:378 μM in the event plume reported in Resing et al. (2011) table S1.

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