Supplementary Information for

Abiotic hydrocarbons discharge from a felsic rock-hosted hydrothermal system

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Supplementary Text

**T1. Geological setting**

The volcanic island Lutao (or Green Island) (22.63°-22.70°N, 121.45°-121.55°E), covering an area of about 17 km2, is located at the northern end of the Luzon arc, 34 km to the southeast of Taiwan island. It is formed by the volcanic activity driven by the subduction of the South China Sea plate beneath the Philippine plate (Fig. S1a) 1. The volcanism occurred in Pleistocene, followed by crustal uplift and seawater erosion of the accumulated stack 2. The volcanic rocks constituting the island range from basalt to dacite but are dominated by andesite with primary mineralogy of plagioclase and amphibole 3,4. Only a few rock samples showed the occurrence of olivine (<5%) and pyroxene (<10%) 5. The MgO and ΣFeO contents of Lutao andesite fall in a range of 2.4 – 6.8% and 4 – 9% (average 6.4%), respectively. According to the chemical compositions of Lutao rock samples 5, the CIPW norm calculation suggested that olivine occurred in 1/3 samples with content of 2 – 7%. The average contents of olivine and pyroxene of Lutao rock was about 1.4% and 5.8%, respectively.

The outer rims of the island are covered by Holocene raised coral reefs (Fig. S1d) 6. The hydrothermal system, named as the Chao-Jih hot springs, situates at the southeastern corner of Lutao (Fig. S1b). There are two characteristic vents within this coral reef covered sediment-starving geothermal field, the Zhudanqu (ZDQ) brine vent and the Huwaichi (HWC) vapor spring (Fig. S1 c). The ZDQ brine vent was protected by concrete walls, forming a shape like a well, discharging vent fluids with a temperature of about 90 oC, pH of about 7.8, and salinity of 36‰. The HWC vapor spring that about 80 m distance from the ZDQ vent, on the contrary, showed vent fluids with a temperature of about 65 oC and pH of about 7.5, and salinity of 29-31‰. Because the gases discharged from the HWC vapor spring may have experienced anaerobic oxidation (see section T4), we will focus on the origin of short-chain alkanes released from the ZDQ brine vent in this study.

**T2. Methane was not originated from the mantle/magma**

CH4 and C2H6 only exist in the mantle/magma with *f*O2 3 log units lower than that of Fayalite-Magnetite-Quartz (FMQ) buffer 7,8. The calculated *f*O2 (10-16 to 10-12 bar) at 645 – 813 oC of andesite, however, was 2 log units higher than that of FMQ 3. Therefore, it is impossible that the Lutao hydrocarbons were directly produced from the mantle/magma, where the C-O-H fluids would be dominated by CO2 and H2O. Besides, the methane isotopologue abundances also suggested that the Lutao methane was produced at a temperature of 174 – 206 oC, rather than the high-temperature conditions of the mantle/magma.

**T3. Modeling**

**1. Model for δ13C fractionation in a closed C-O-H system (Fig. 3)**

(1) No matter the methane was produced from a one-step reaction or a two-step process, the overall formation mechanism is the reaction (3) in the main text, buffered by Fe(II) minerals (e.g., fayalite) and Fe(III)-bearing minerals (e.g., magnetite, hematite). The chemical equilibrium of C-O-H fluid under this environment has been studied extensively by 9,10. They proposed that the chemical ratio between equilibrated CH4 and CO2 is a function of temperature:

log10 (CH4/CO2) = 5280/*T* -11.12 = *a* (1)

where *T* (K) is the equilibrium temperature.

(2) In a confined environment like fluid inclusion, CH4 was completely conversed from CO2. The conversion ratio (*CR*) of CO2 to CH4 is:

*CR* = 10*a*/(1+10*a*) (2)

(3) According to Horita (2001) 11, the carbon isotope exchange in the CO2-CH4 system is:

103lnα(CO2−CH4) = 0.16+11.754∗(106/T2) − 2.3655∗(109/T3) + 0.2054∗(1012/T4) (3)

(*T* = 273 – 1573 K)

(4) Based on the isotopic mass balance:

δ13C(CO2)*t* \*(1-*CR*) + δ13C(CH4) \**CR* = δ13C(CO2)*i* (4)

whereδ13C(CO2)*i* andδ13C(CO2)*t* are the initial δ13C(CO2) and that at equilibrium, respectively.

then,

δ13C(CO2)*t* - *CR* \*(δ13C(CO2)*t* - δ13C(CH4)) = δ13C(CO2)*i* (5)

Because δ13C(CO2)*t* - δ13C(CH4) ≈ 103lnα(CO2−CH4), then,

δ13C(CH4) ≈ δ13C(CO2)*i* - 103lnα(CO2−CH4) + 103lnα(CO2−CH4)\**CR* (6)

One disadvantage is that CO2 in the Lutao gas samples was in trace amount, similar to many low-temperature continental gas seeps 12,13. The low CO2 content was caused by either high CO2-CH4 conversion ratio at low temperatures or removal by the vent fluids, or a combination of both. Therefore, we don’t know the initial δ13C(CO2) values and δ13C(CO2) at equilibrium. In this study, we set the initial δ13C value of magmatic CO2 at a range of 0 ~ -8‰ 14,15. Two temperature ranges could generate δ13C(CH4) of -15.5 ~ -19‰: 180 ~ 206 oC and > 408 oC, where the former range fits well with the methane isotopologue results.

Numerous studies have investigated the δ13C(CH4) values and their equilibration temperatures with CO2, using the equation suggested by Horita (2001) 11. However, the conversion ratio from CO2 to CH4 in the C-O-H system is less than 5% at temperatures of >265 oC. The δ13C values of the residual CO2 will be almost identical to the initial values at this temperature range. As a result, the equilibration temperature calculated from CO2-CH4 isotopic equilibrium will always fit our proposed model. Consequently, we only chose the data with temperatures calculated using other methods such as chemical equilibrium, methane isotopologue abundances, and D/H equilibrium.

**2. Model for D/H fraction in a closed C-O-H system (Fig. S7)**

(1) No matter the CH4 was exclusively produced from respeciation of C-O-H fluids (equation 20) or a combination of serpentinization and Sabatier reaction (equations 22 and 24), the stoichiometric ratio between CO2: H2O: CH4 is 1:2:1. A simplified expression of the reaction could be:

CO2 + 2H2O 🡪 CH4 (7)

The initial magmatic H2O/CO2 molar ratio is named as *RH*, which varies greatly with different systems 16, but is basically higher than 2.

(2) When the C-O-H fluid achieved chemical equilibrium buffered by typical volcanic rocks 9,10, the ratio between CH4 and CO2 is:

log10 (CH4/CO2) = 5280/*T* -11.12 = *a* (8)

where *T* (K) is the equilibrium temperature.

Because CH4 was completely conversed from CO2, therefore, the conversion ratio (*CR*) of CO2 to CH4 is:

*CR* = 10*a*/(1+10*a*) (9)

According to the stoichiometric ratio of the reaction (9), the conversion ratio of H2O is 2\**CR/RH.*

(3) The D/H fractionation between CH4, water vapor, and H2 has been well studied by 17,18:

CH4(g)/H2(g): *α1* = 0.8994 + 183540/*T*2 (10)

H2O(g)/H2(g): *α2* = 0.9714 + 225230/*T*2 (11)

Combined with equations (12) and (13), the fractionation between CH4(g) and water vapor will be:

*α* = *α1* / *α2* (12)

Then, δ2HCH4 - δ2HH2O = *ε*CH4-H2O = (*α* – 1)\*1000 (13)

(4) Based on the isotopic mass balance:

δ2HH2O*i* = δ2HH2O*t*\* 2\*(1-2\**CR/RH) +* δ2HCH4*t*\* 4\**CR/RH* (14)

therefore, δ2HCH4*t*= [δ2HH2O*i\*RH + ε*CH4-H2O \*(2*RH*-4*CR*)]/2*RH* (15)

the subscript *i* and *t* denote the initial δ2H value and that at equilibrium, respectively.

The modeled results (Fig. S7) indicate that at a temperature of < 250 oC, the resulting δ2HCH4 values vary significantly with initial magmatic H2O/CO2 ratios. At higher temperatures of > 250 oC, on the contrary, the δ2HCH4 values are almost identical with different initial *RH* ratios. The initial δ2H value of magmatic water vapor was set at 0 ~ - 50‰ 15. The relatively faster D/H exchange between CH4, H2, and H2O with respect to 13C/12C exchange restricts the application of this model. Nevertheless, the methane released from Pantelleria, Chimaera, Nisyros, Zambales generally follows the estimated gray bands.

**T4. Geochemistry of methane that discharged from the HWC vapor spring**

In this study, the gas from the HWC vapor spring was also collected and analyzed for chemical and stable isotopic compositions (**Table S3**). When compared with the gas samples from the ZDQ brine vent, the HWC gas samples showed relatively higher N2 contents but lower CH4 concentrations (46.35 mmol/mol). Both vents showed similar concentrations of all the other chemical components. A remarkable difference between the methane discharged from both vents is that the HWC samples presented significantly heavier δ13C (-8.08±1.97‰) and δ2H (-2.34±43.55‰) values. Two mechanisms were applied to explain this phenomenon.

**(1) Microbial oxidation**: Both the ZDQ and HWC methane was originated from the same source, while the HWC methane experienced extensive microbial oxidation. The most compelling evidence for this hypothesis is that the δ13C(CH4) values of Lutao gas samples increased linearly with their δ2H values (Fig. T1). The slope of 2H/13C fractionation (ΔH/ΔC) is 10.1, close to the reported values for aerobic oxidation of methane 19,20. In addition, two HWC gas samples showed δ13C and δ2H values just on the oxidation curve, further suggested that the methane in these samples might originate from the ZDQ gas and subsequently underwent microbial oxidation with different degrees.

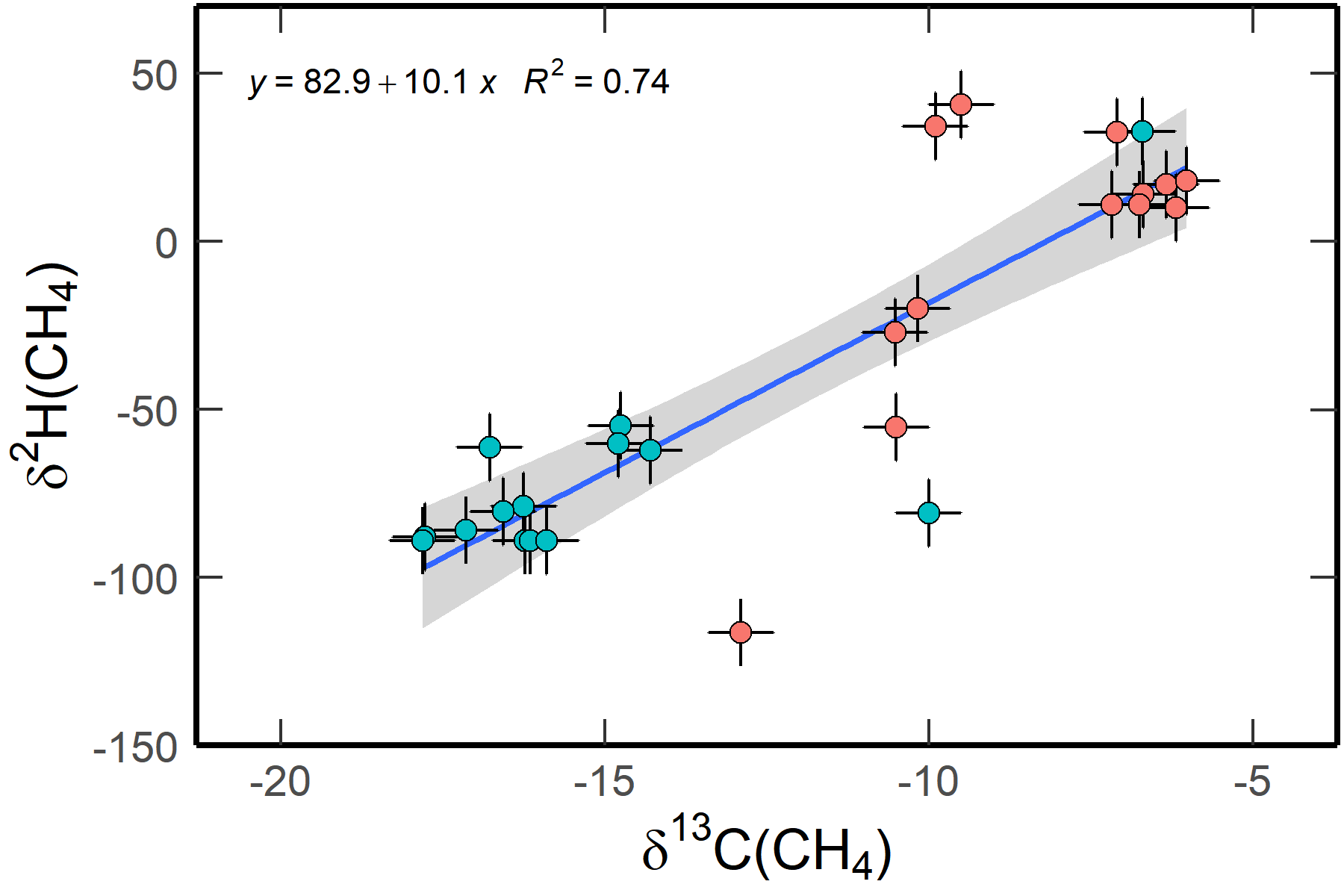


Fig. T1: δ2H - δ13C plot of methane discharged from ZDQ brine vent (blue circles) and HWC vapor spring (red circles), respectively. Unit: δ13C, ‰, vPDB; δ2H, ‰, vSMOW.

However, an **(2) enhanced conversion from CO2 to CH4 in the C-O-H system** will also result in both elevated δ2H and δ13C values. In a closed equilibrated C-O-H system, the conversion ratio of CO2 to CH4 decreases with temperature. As a result, the δ13C values of the remnant CO2 become increasingly heavy with decreasing temperature. Although the fractionation factor between CO2 and CH4 (ΔCO2-CH4) generally increases with decreasing temperature 11, the δ13C values of the resulting CH4 increases with declining temperatures, and eventually close to the initial δ13C(CO2) values (Fig. 3). For example, at 180 and 104 oC (the apparent formation temperatures of methane discharged from the ZDQ brine vent and HWC vapor spring, respectively. Temperatures were calculated from the Δ13CH3D abundance, Table 2), the conversion ratios of CO2 at equilibrium are 77.44% and 99.87%, respectively 10. This result is consistent with the low CO2 contents in the Lutao gas samples, as well as the low-temperature gas seeps in Chimaera and Zambales 12,21–23. Nevertheless, the δ13C values of CO2 in these fields were quite negative, possibly ascribed to the fact that the residual CO2 was in trace amount or has been massively removed by the alkaline vent fluids. The detected CO2 was primarily a product of methane oxidation.

According to the relationship between temperature and equilibrated δ13C(CH4) values (Fig. 3), the C-O-H system equilibrated at 180 and 104 oC would eventually create ultra-heavy δ13C values of remnant CO2 of 20‰ and 41‰, respectively, when the initial δ13C of magmatic CO2 was -8‰. As a result, the δ13C values of generated CH4 will be -16.7 and -8.1‰, respectively. Both values resemble the δ13C values of methane discharged from the ZDQ brine vent (-19 ~ -15.5‰) and HWC vapor spring (-10 ~ -6‰). A similar process also applies to the D/H fractionation between CH4 and H2O (Fig. S7), where the δ2H values of Lutao methane fit well with the modeled results.

Furthermore, the Δ13CH3D abundance of the HWC methane was 3.61 – 4.02‰, significantly larger than that of ZDQ methane (2.38 - 2.74‰). This result contradicts previous studies on the aerobic oxidation of methane, where the Δ13CH3D abundance decreased with enhanced oxidation 20. The effect of anaerobic oxidation on the methane isotopologues, however, was less constrained. Some studies suggested that it could induce partial carbon isotope equilibration between residual methane and CO2 24. Therefore, it is possible that the apparent temperature of HWC methane (93 - 115 oC) reflects the temperature of anaerobic oxidation 21. Thermophilic anaerobic bacteria were atypical but existed. A previous study reported a hyperthermophilic methanogen could survive at 122 oC and produce CH4 with heavy δ13C values 25.

The methane oxidation curve (Fig. T2) also supports that the methane in most HWC samples was not an oxidation product of the ZDQ methane. The δ13C(CH4) - CO2/CH4 diagram of methane in the ZDQ samples and several HWC samples follows the theoretical oxidation curves with initial δ13C(CH4) values of -19 ~ -15.5‰ and ΔCO2-CH4 of -30‰. It is suggested that the methane in some HWC samples was oxidized from the ZDQ methane. The majority of HWC samples, however, showed different oxidation curves than the ZDQ samples, indicating that they were originated from different sources or have experienced diverse processes. The endmember δ13C value of HWC methane could be determined as -10 ~ -8‰.

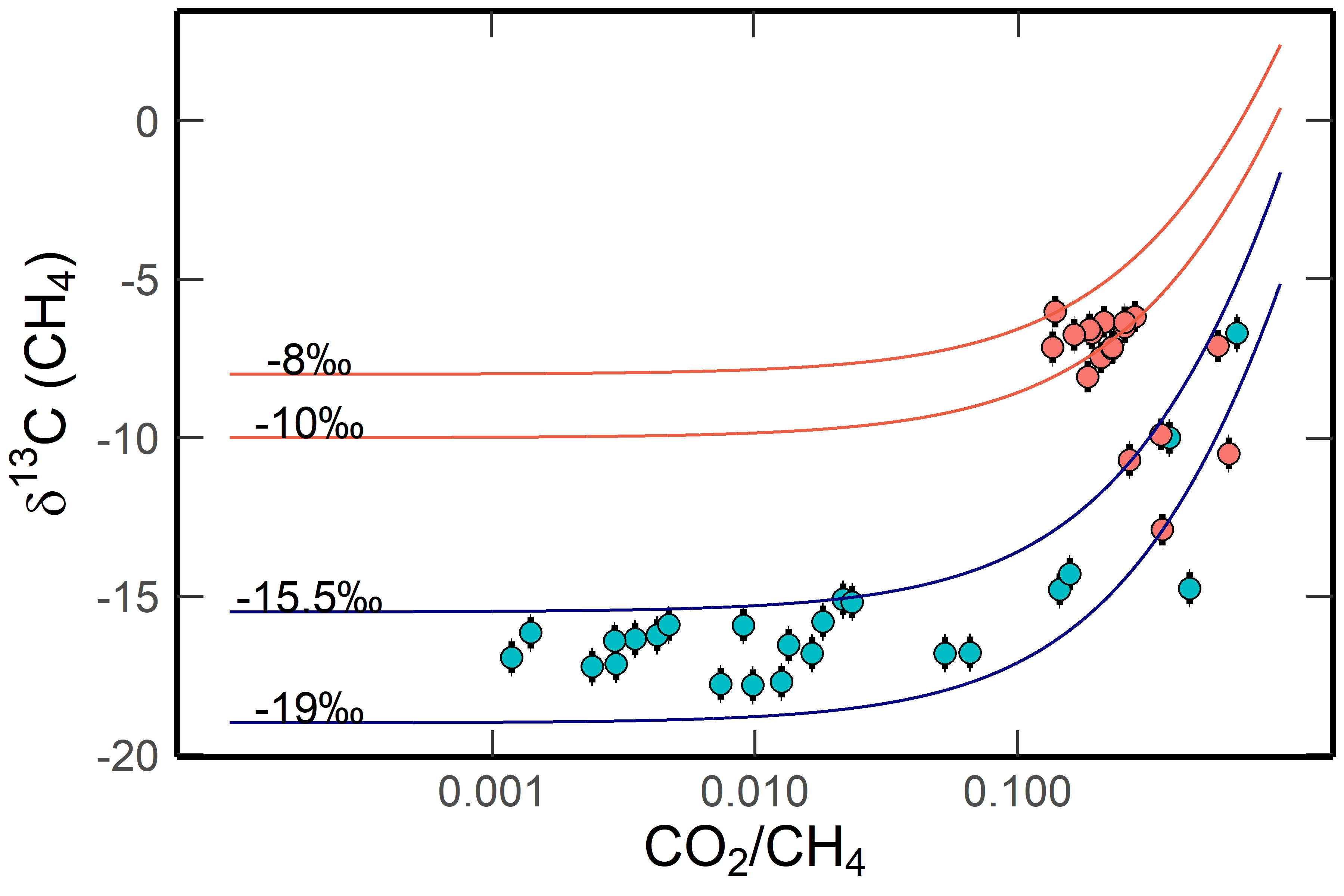


Fig. T2 Variations of δ13C(CH4) values of methane discharged from the ZDQ brine vent (blue circles) and the HWC vapor spring (red circles), respectively. The initial δ13C(CH4) value of each line was marked on the plot. The theoretical curves were calculated using equation (27), using a fractionation factor ΔCO2-CH4 of -15‰ (red lines) or -20‰ (blue lines). Partial dissolution of CO2 has been considered, which dissolved 60% ZDQ CO2 and 67% HWC CO2 into the fluid phase.

Furthermore, the δ13C - CH4/(C2+C3) plots of Lutao methane and ethane clearly distinguish the trends of microbial oxidation from the mixing between the HWC and ZDQ gases (Fig. T3). The initial CH4/(C2+C3) ratio of the ZDQ gas samples was about 200 – 230. With enhanced microbial oxidation, the methane was gradually consumed, resulting in simultaneously decreased CH4/(C2+C3) ratios and increased δ13C values. The CH4/(C2+C3) ratio of the HWC samples, on the contrary, was elevated to about 700 – 800. Because the ZDQ ethane exhibited increased δ13C values with almost constant CH4/(C2+C3) ratios, it is indicated that microbial oxidation of ethane posed minor influence on the CH4/(C2+C3) ratios. Therefore, the enlarged CH4/(C2+C3) ratios of the HWC gases did not result from ethane oxidation. Some HWC samples exhibited CH4/(C2+C3) ratios of about 300 – 400 and δ13C(CH4) values of -13 ~ -8%. These samples could be explained as mixtures of the HWC and ZDQ gases, which were subsequently oxidized by microbial activities.

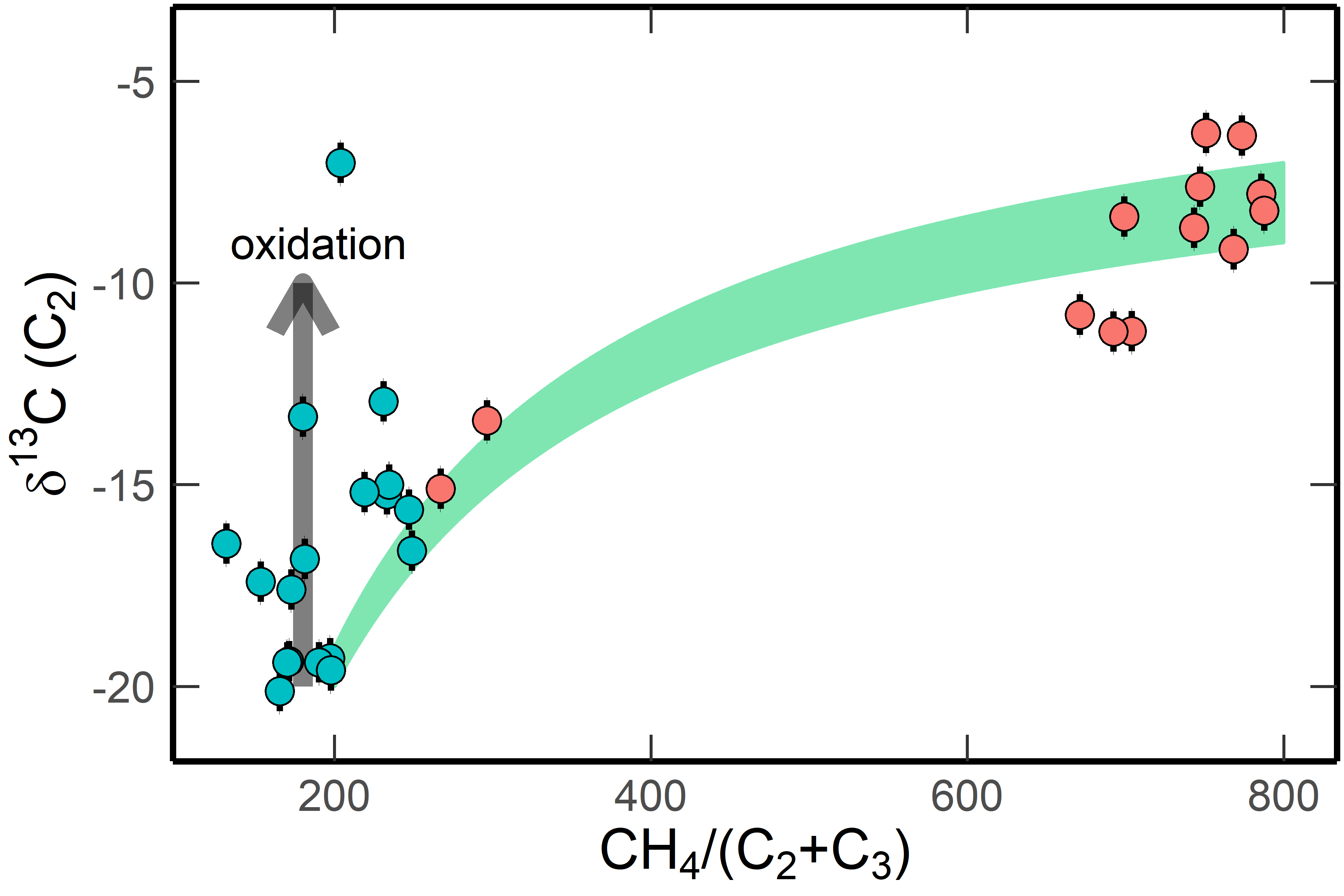
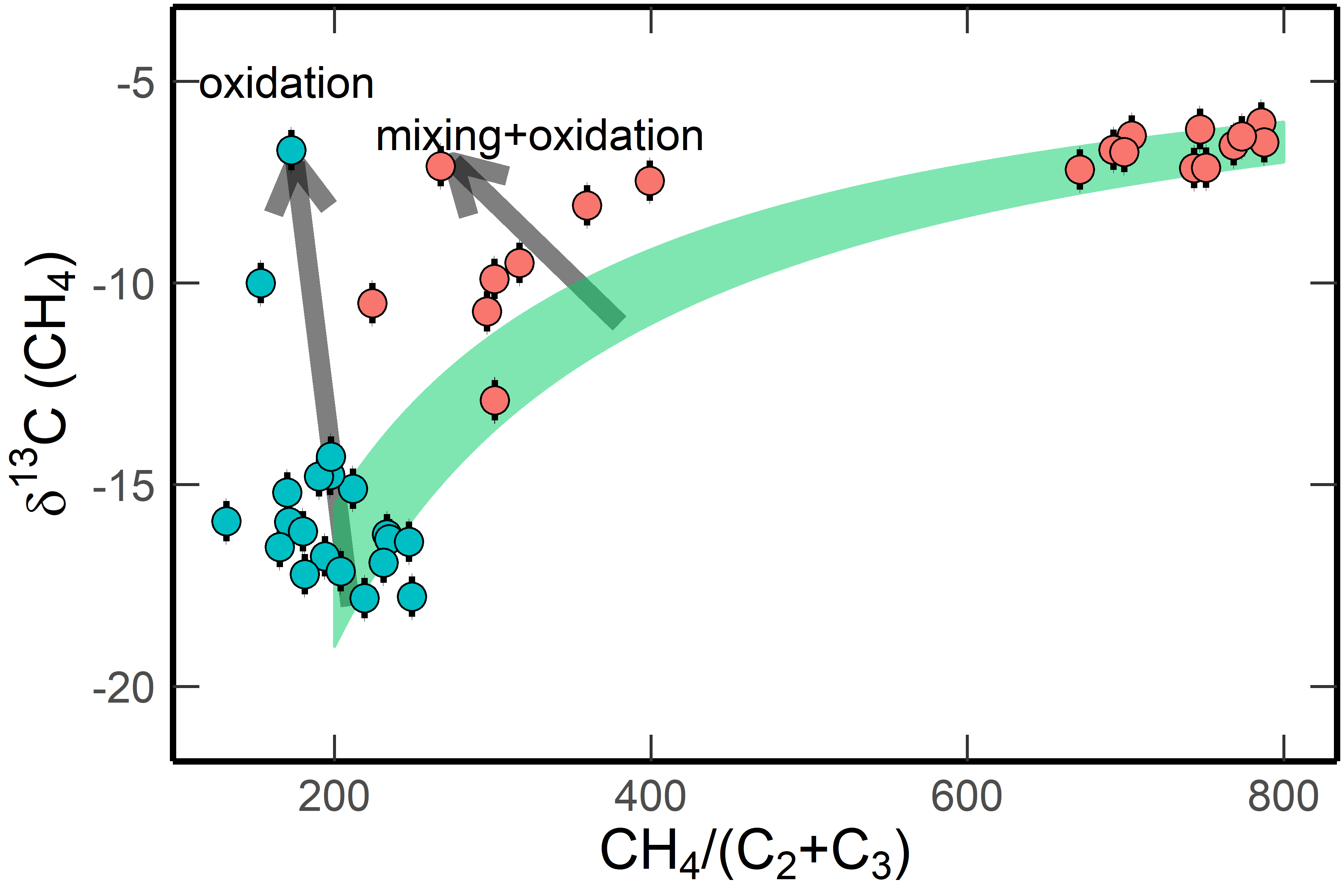


Fig. T3 δ13C – CH4/(C2+C3) plots for (a) methane and (b) ethane discharged from the ZDQ brine vent (blue circles) and HWC vapor spring (red circles). The mixing curves (green bands) were calculated using the following endmembers: HWC, δ13C(CH4) = -7 ~ -6‰, δ13C(C2) = -9 ~ -7‰, CH4/(C2+C3) = 800; ZDQ, δ13C(CH4) = -19 ~ -15.5‰, δ13C(C2) = -20 ~ -19‰, CH4/(C2+C3) = 200.

In conclusion, multiple pieces of evidence suggested that the heavy δ13C and δ2H values of HWC methane were not created by microbial oxidation. The methane released from the HWC vapor spring was probably leached from fluid inclusions that equilibrated at about 100 oC in the host rock. Nevertheless, potential oxidation that occurred during hydrothermal circulation was still largely unknown, and the impact of anaerobic oxidation was not constrained. Therefore, we would like to present the source of the short-chain alkanes discharged from the HWC vapor spring in the supporting information rather than in the main text.

**T5. Flux estimation**

In this study, we roughly estimated the flux of abiogenic methane that discharged from the Lutao geothermal system.

1. During our sampling, Lutao gas filled the sampling bottle with a volume of about 100 mL within 20 s. The sampling bottle was connected to a glass funnel with a cross-sectional area of 175 cm2. Because the venting area of ZDQ is about 1 m2; the total gas flux of the ZDQ vent was estimated at 285 mL s-1.
2. The CH4 content of the Lutao gas was 11% ~ 17%. Therefore, the methane flux was about 31-48 mL s-1. That is about 1000 – 1500 m3 *a*-1, or 700 – 1080 kg *a*-1.
3. The vent fluids filled a volume of 0.8 m3 in about 5 s. Therefore, the fluid flux was calculated as 160 L s-1. Because the density of the vent fluids closes to 1 g cm-3, the annual flux of Lutao vent fluid is about 5000\*106 kg *a*-1.
4. The W/R ratio of the Lutao system was calculated as about 2 based on the boron concentrations (1.10 -1.20 mM L-1) of the vent fluids. Therefore, the annual consumption of host rock is about 2500 \*106 kg, corresponding to a volume of 8.1 ~ 9.6 \*10-4 km3 according to the density of intermediate rock (2.6 – 3.1 kg L-1). Because the Lutao island covers an area of about 17 km2 and at 50 m water depth about 60 km2, a 13 - 16 m thick host rock could easily sustain the release of abiogenic methane for 1000 years.
5. Consequently, the mass ratio between the Lutao host rock and methane is estimated at 2.3 ~ 3.6 \*106. This value is comparable to the range of published data for methane-rich inclusions in the plutonic rocks of Southwest Indian Ridge (0.3 ~ 0.6 mmol methane/kg, or a mass ratio of 1 - 2\*105) 26, Cayman ultramafic rocks (4.3 nmol/g, or a ratio of 1.5\*107), and Zambales ophiolite (2 ~ 37 nmol/g, or a ratio of 1.6 ~ 31\*106) 27.

**T6. Thermodynamic calculation:**

According to the structure and nature of methane, a carbon source, a hydrogen source, and a reductive environment are required to form methane. Under natural hydrothermal systems, carbon source could be carbonate, CO2, CO, C, or organic acids. The abundance of CO is below the detection limit in the Lutao system and therefore, was not considered. Etiope and Whiticar (2019) 13 concluded that organic acids such as formic acid and formate are intermediate products rather than carbon sources for abiotic CH4 production. Therefore, potential carbon source for Lutao methane was CO2, C, or carbonate. Typical hydrogen sources are H2O and H2. The reductive environment is usually supplied by H2 or rock buffer (Fe2+-bearing minerals).

Under these statements, potential processes to abiotically produce methane include:

(1) Carbonate reduction 28:

12FeO + CaCO3 + 2H2O = 4 Fe3O4 + CH4 + CaO (16)

This process has been suggested to produce methane in the mantle at temperatures of 500 – 1500 oC and pressures of 5 – 11 GPa.

(2) respeciation of C-O-H fluids 10,29: If the carbon source was CO2 (which is quite common in hydrothermal systems) rather than carbonate, then the equation (18) transfers to:

CO2 + 2H2O = CH4 + 2O2 (17)

However, this reaction is thermodynamically unfavorable at all temperature ranges. A reductive agent was required to overcome the thermodynamic barrier. In volcanic rocks, Fe2+ the most common reductive agent.

12FeO + CO2 + 2H2O = CH4 +4Fe3O4 (18)

or, 8Fe3O4 + CO2 + 2H2O = CH4 + 12Fe2O3 (19)

If CO2 was absent, this reaction resembles the simplified form of the serpentinization process that generates H2 30,31:

3FeO + H2O = H2 + Fe3O4 (20)

where FeO represents the ferrous components of silicate minerals such as olivine and pyroxene 32,33.

(3) The most widely studied mechanism for the production of abiotic methane is Fischer-Tropsch-Type reaction (equation 23), or its one-step form (Sabatier reaction, equation 24) 13,29,34,35. Both processes require H2 as a reactant.

CO2 + (2+m/2n)H2 = (1/n)CnHm + 2H2O (21)

CO2 + 4H2 = CH4 + 2H2O (22)

If the carbon source was C or carbonate, then the reactions will be:

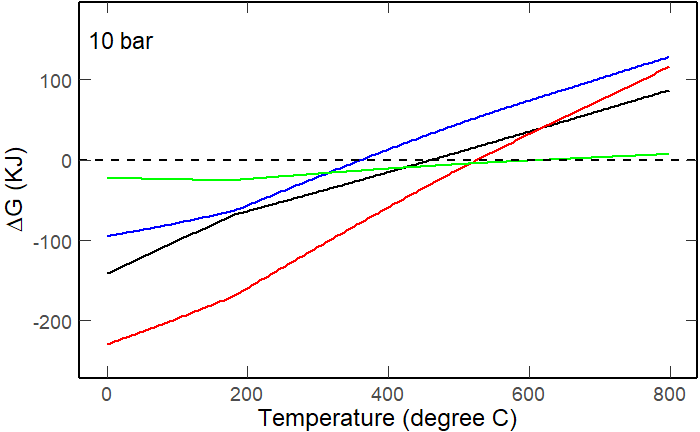
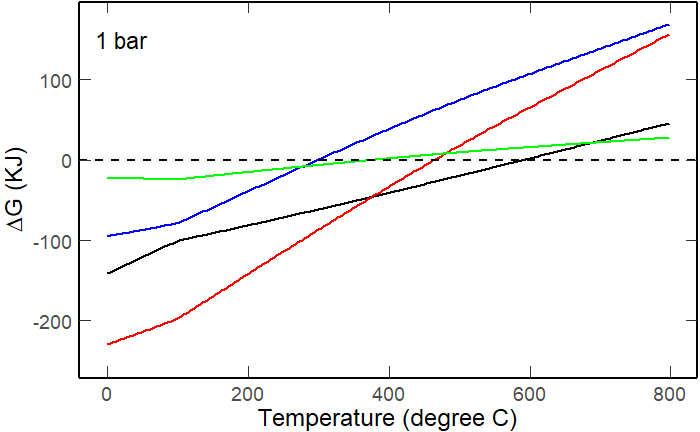
C + H2 = CH4 (23)

MCO3 (M = Fe, Ca, or Mg) + 4H2 = CH4 + MO + 2H2O (24)

Thermodynamic calculations using *R* package CHNOSZ 36–38 suggested that the equations 19 and 21 are thermodynamically unfavorable at temperatures of 0 -1000 oC and pressure of 1 – 500 Bar. Equation 26 could occur only at temperatures of < 25 oC. Equation 25 is a less plausible process to generate Lutao methane because graphite is not common in andesitic volcanic rocks.

For the rest equations 18, 20, 22, and 24, Fig. T4 compiles the changes of ΔG of these equations at different temperatures and pressures. At 1 bar, equation 20 (C-O-H respeciation) exhibits the most negative ΔG values at temperatures < 380 oC, and therefore is the most thermodynamically favorable reaction at this temperature range. Equation 24 (Sabatier reaction) is more favorable at 380 – 590 oC. Beyond this temperature, both reactions are thermodynamically unfavorable. Equation 18 (carbonate reduction) only favorable at temperatures < 308 oC, while equation 22 (serpentinization) shows slightly negative ΔG values at < 380 oC. At a pressure of 10 bar that represents a shallow depth environment, C-O-H respeciation is always the most favorable reaction in case of ΔG < 0, followed by Sabatier reaction and carbonate reduction. At 500 bar that typically used in laboratory experiments to study the serpentinization and abiotic formation of methane 39,40, C-O-H respeciation is still the thermodynamically most favorable reaction at < 580 oC. Beyond this temperature, serpentinization prevails.

Based on these calculations, the abiogenic methane discharged from the Lutao field was potentially produced by two routes: (1) one-step formation: methane was exclusively generated from the respeciation of C-O-H fluids, which is the most thermodynamically favorable reaction at temperatures ranging from 0 to 580 oC. Presumably, magmatic CO2 and H2O were trapped in the intrusive rocks during Lutao volcanism; these C-O-H fluid inclusions reacted with Fe2+ in the surrounding rock to form methane. Although the Lutao host rock is dominated by andesite, the sporadic occurrence of ultramafic minerals (olivine and pyroxene) and the absence of ferric minerals suggested that the Lutao host rock contains 4 – 9% FeO 3,5. (2) Two-step reactions: Serpentinization is the most favorable reaction at high pressure (500 Bar) and high temperatures (> 580 oC). However, olivine is stable at temperatures > 400 oC. Therefore, it is plausible that serpentinization occurred firstly during the initial cooling of Lutao magma when temperatures colled to < 400 oC. Although the reaction rate of serpentinization highly relies on kinetic parameters, it is suggested that serpentinization is a fast process on the geological time scale 31. The produced H2, together with magmatic CO2 and H2O were trapped in the intrusive rocks and formed fluid inclusions. Then these CO2-H2-H2O rich inclusions achieved equilibrium via Sabatier reaction (equation 24) or respeciation (equation 20), or a combination of both processes at lower temperatures and pressures. The sluggish kinetic barrier of Sabatier reaction without catalysts was overwhelmed by the geological time scale 41 since the major volcanic eruptions at Lutao occurred at 1.3 Ma. Most H2 and CO2 have been transferred to CH4 when equilibrated at low temperatures, that CH4-rich H2-free inclusions have been suggested by previous studies 26,41. In addition, both species may be additionally removed by microbial oxidation or carbonate precipitation during hydrothermal circulation 19,42. Therefore, both gases were not detected or at low contents in the Lutao gas samples.



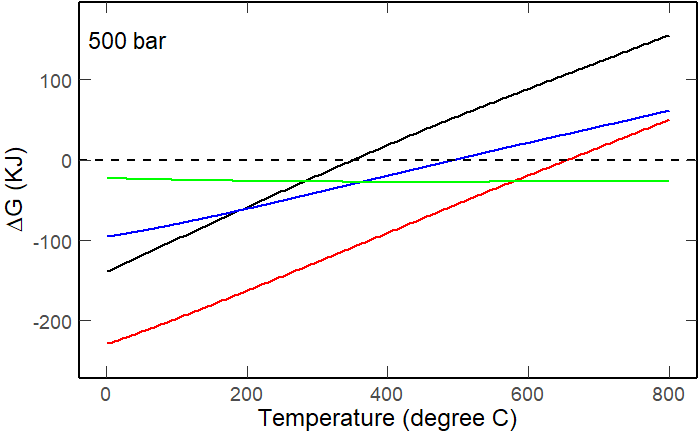


Fig. T4 Variations of Gibbs free energy changes (ΔG) as a function of temperature from 0 to 800 oC, with pressure conditions of 1 bar, 10 bar, and 500 bar. Black line: Sabatier reaction (equation 24); blue line: carbonate reduction (equation 18); red line: respeciation of C-O-H fluids (equation 20); and green line: serpentinization (equation 22).

Fig. S1

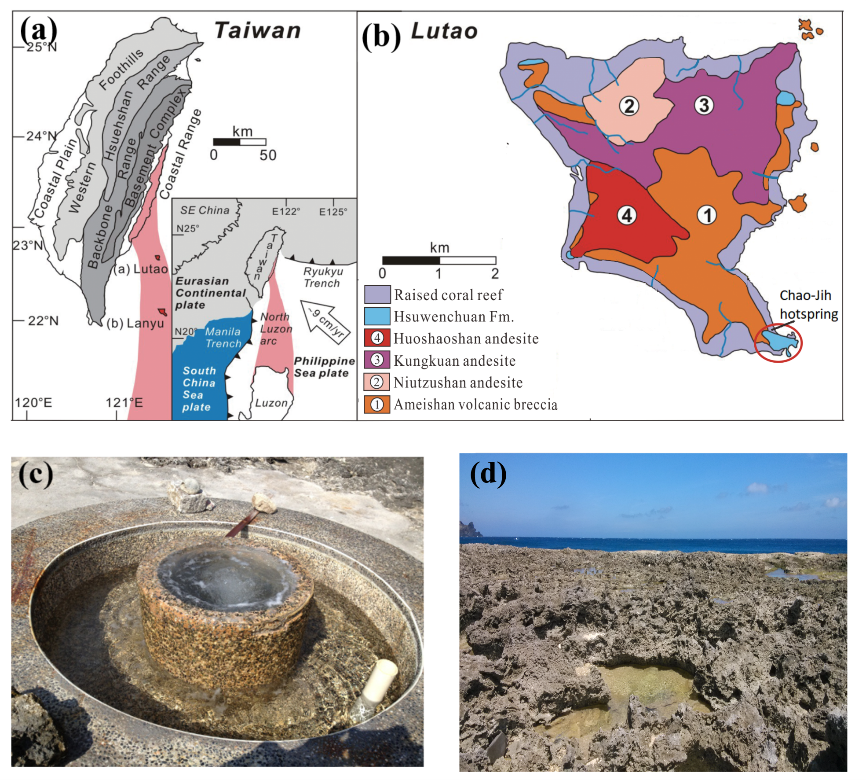


Fig. S1 The Lutao andesite-hosted geothermal system: (a) geological setting, (b) the surface lithology modified from Shao et al., (2014) 1. The island is mostly composed of andesite agglomerate and lava with dominant mineralogy of amphibole and plagioclase. (c) the typical “Zhudanqu” spring, and (d) the modern coral reef covering the geothermal field 6.

# Fig. S2

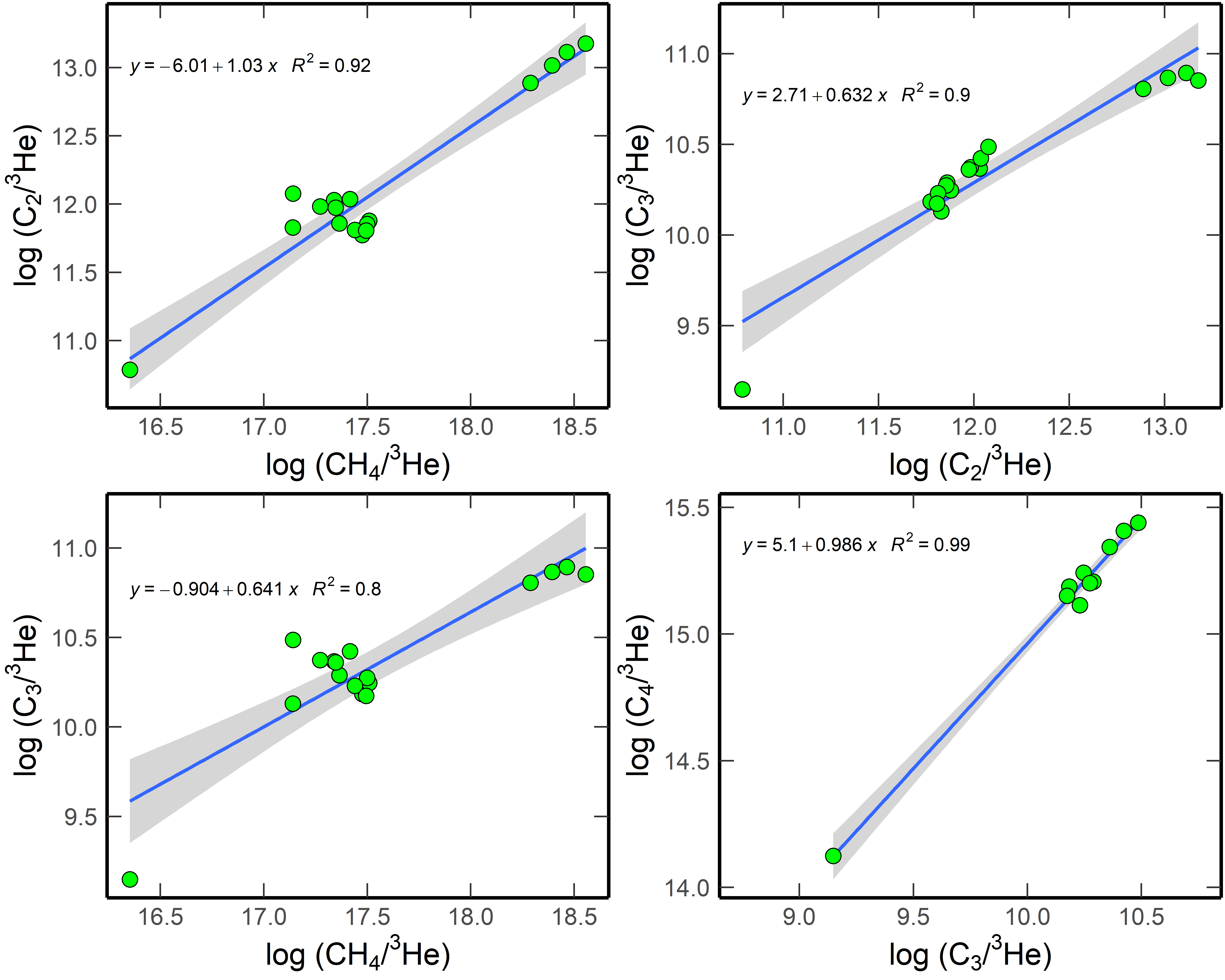


Fig. S2 The relationships between methane, ethane, propane, and butane. 3He was used as a reference to show the relative abundances of Lutao alkanes because 3He was almost exclusively originated from the mantle on account of the dramatically high 4He/20Ne ratios of Lutao gases (Table S1) 43,44.

# Fig. S3

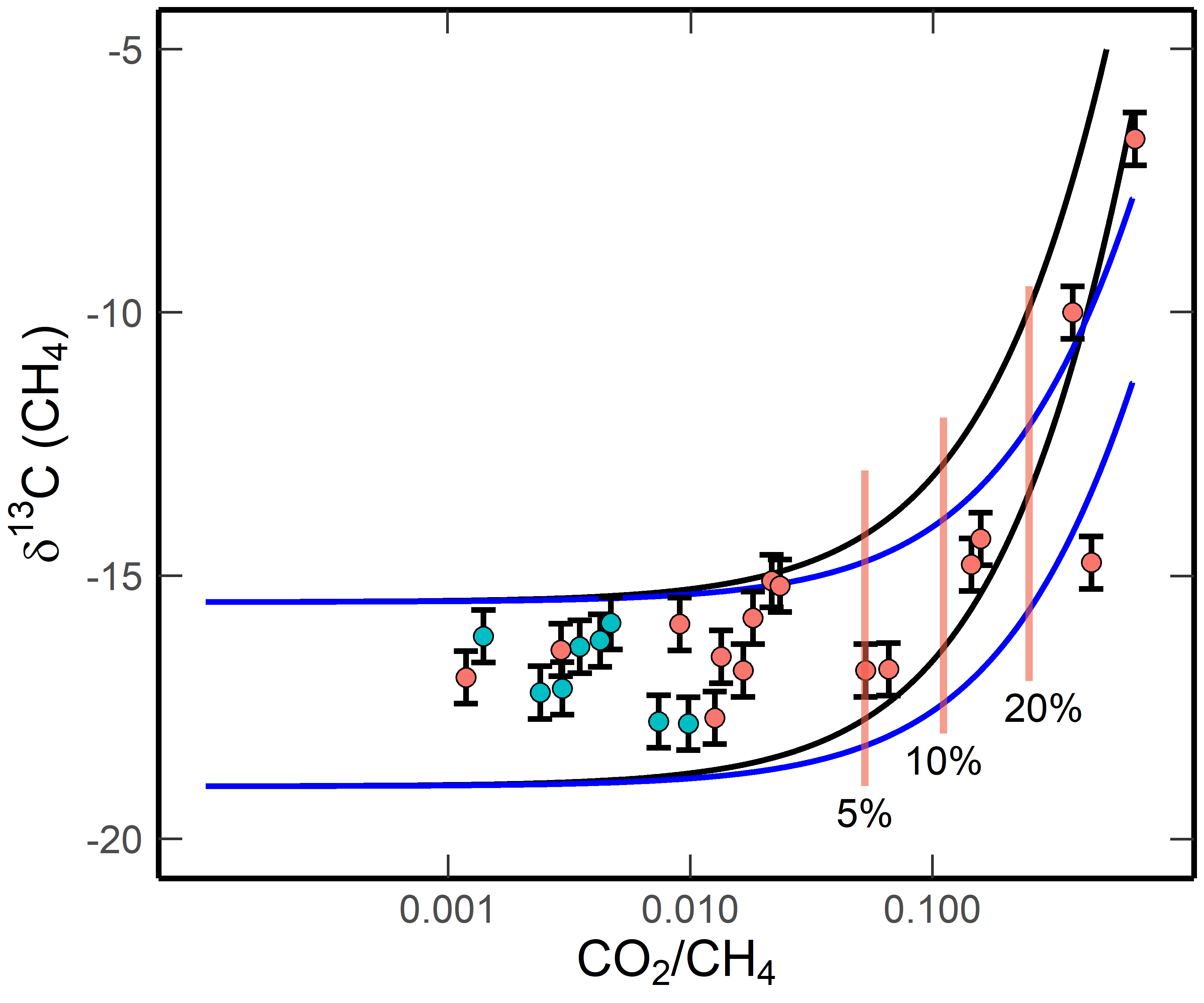


Fig. S3 The correlation between CO2/CH4 ratios and δ13C(CH4) values (per mil, v-PDB) suggesting that methane was oxidized to produce CO2 in the Lutao system. Blue points: HgCl2 was added to prevent microbial oxidation. Red points: HgCl2 was not added.

The theoretical curves were calculated according to Whiticar (1999)19 using the following equation:

δ13C(CH4)*t* = δ13C(CH4)*i* + ΔCO2-CH4 \*ln (1-*F*) (25)

Where the subscripts *i* and *t* denote the initial δ13C(CH4) value and at time *t*, respectively. ΔCO2-CH4 is the 13C isotopic fractionation factor between CO2 and CH4, which covered a large range from -5 to -30‰ 19,45,46. In this study, this value was set at -15‰ (blue lines) or -25‰ (black lines). *F* is the conversion ratio from CH4 to CO2. The initial δ13C(CH4) values were set at a range of -15.5‰ ~ -19‰, respectively. CH4-CO2 conversion ratios (that calculated from the CO2/CH4 ratios) of 5%, 10%, and 20% were marked on the figure. Most samples showed very low conversion ratios, and only the samples without adding HgCl2 solutions experienced significant microbial oxidation. It is suggested that microbial oxidation of methane occurred after sampling/during preservation. CO2 in the samples may have experienced partial dissolution in the vent fluids with a pH of about 7.8 and temperature of 90 oC. Therefore, the total CO2 content will be 2.5 times higher than the residual CO2 in the gas phase.

# Fig. S4

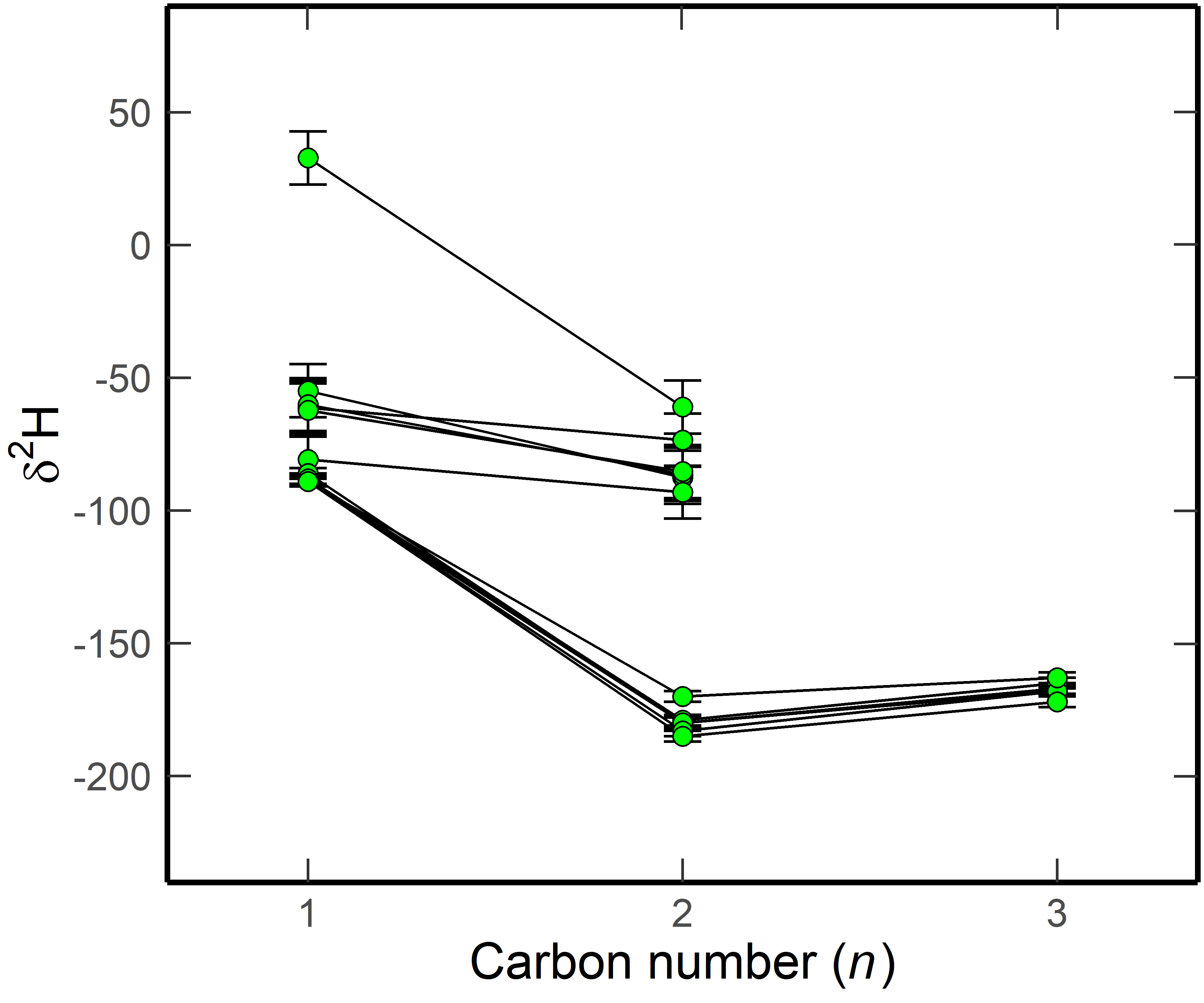


Fig. S4 Reversed trend of δ2H values (per mil, vSMOW) of Lutao alkanes with increasing carbon number (*n*).

# Fig. S5

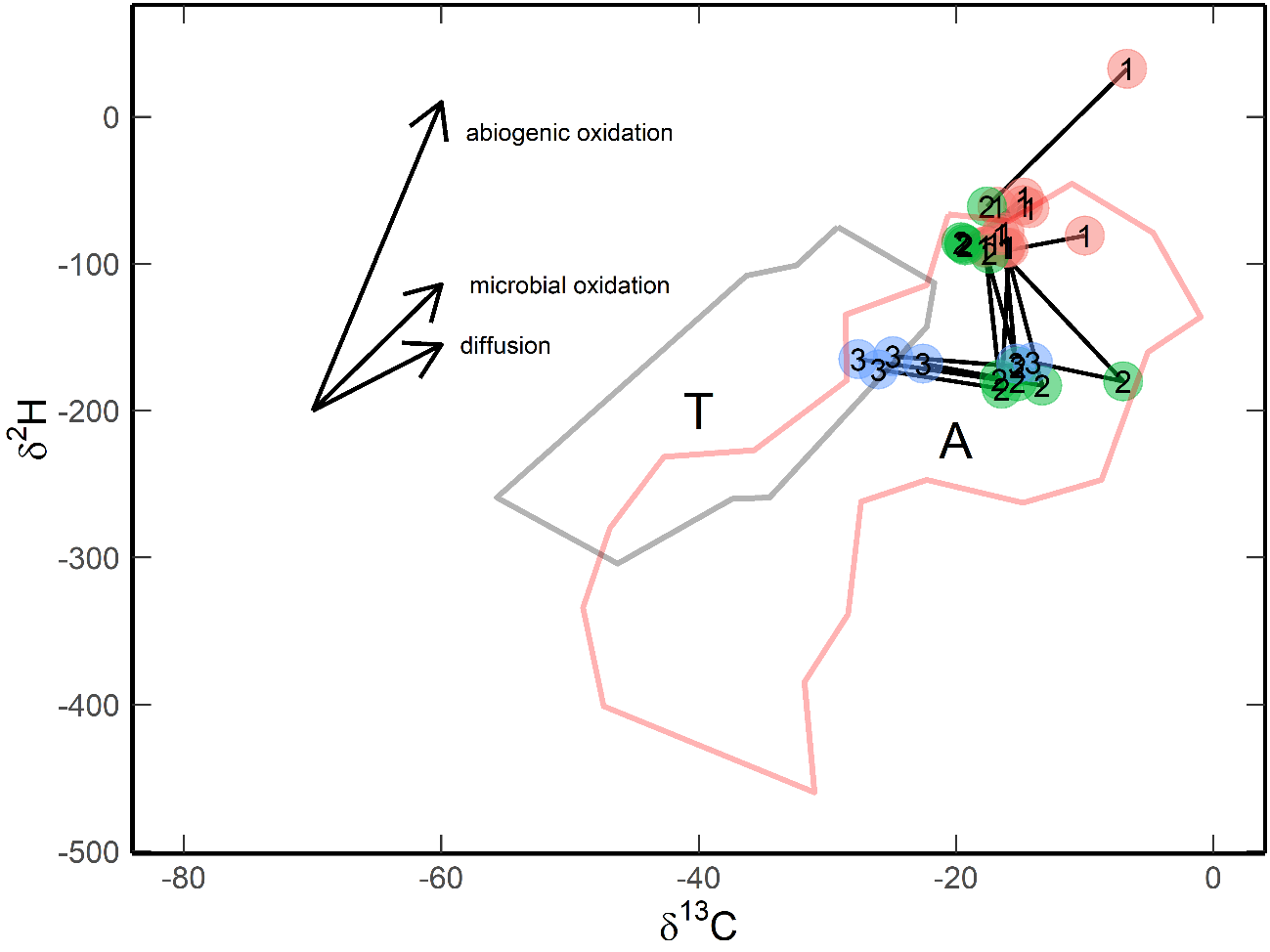
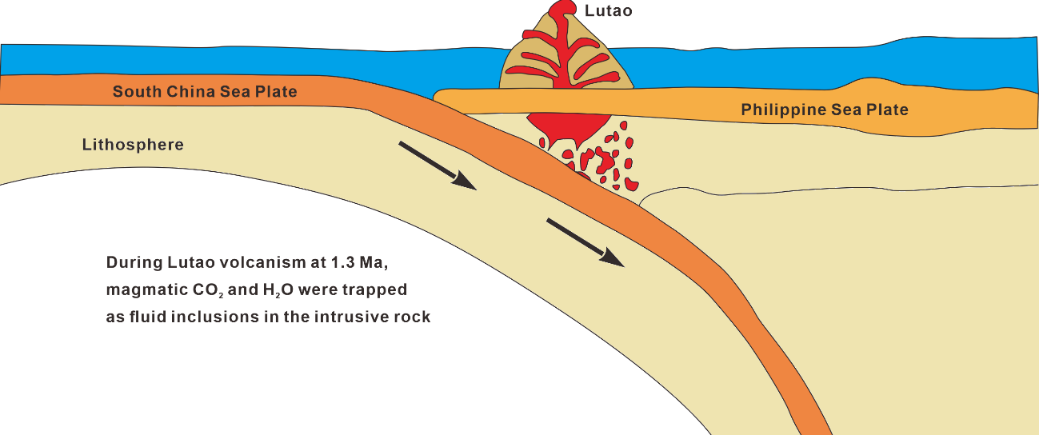


Fig. S5 δ13C – δ2H (CD) diagram of the Lutao alkanes. The numbers inside the dots indicate the carbon number of the alkanes. Isotopic fractionation trends of methane by abiogenic oxidation (ΔH/ΔC = 21), microbial oxidation (ΔH/ΔC = 8.6), and diffusion (ΔH/ΔC = 4.5) were calculated according to Etiope and Lollar (2013) 29 and references therein. The boundaries for thermogenic (T) and abiogenic (A) methane were also suggested by Etiope and Lollar (2013) 29. Units: per mil, vPDB for δ13C, and vSMOW for δ2H.

# Fig. S6



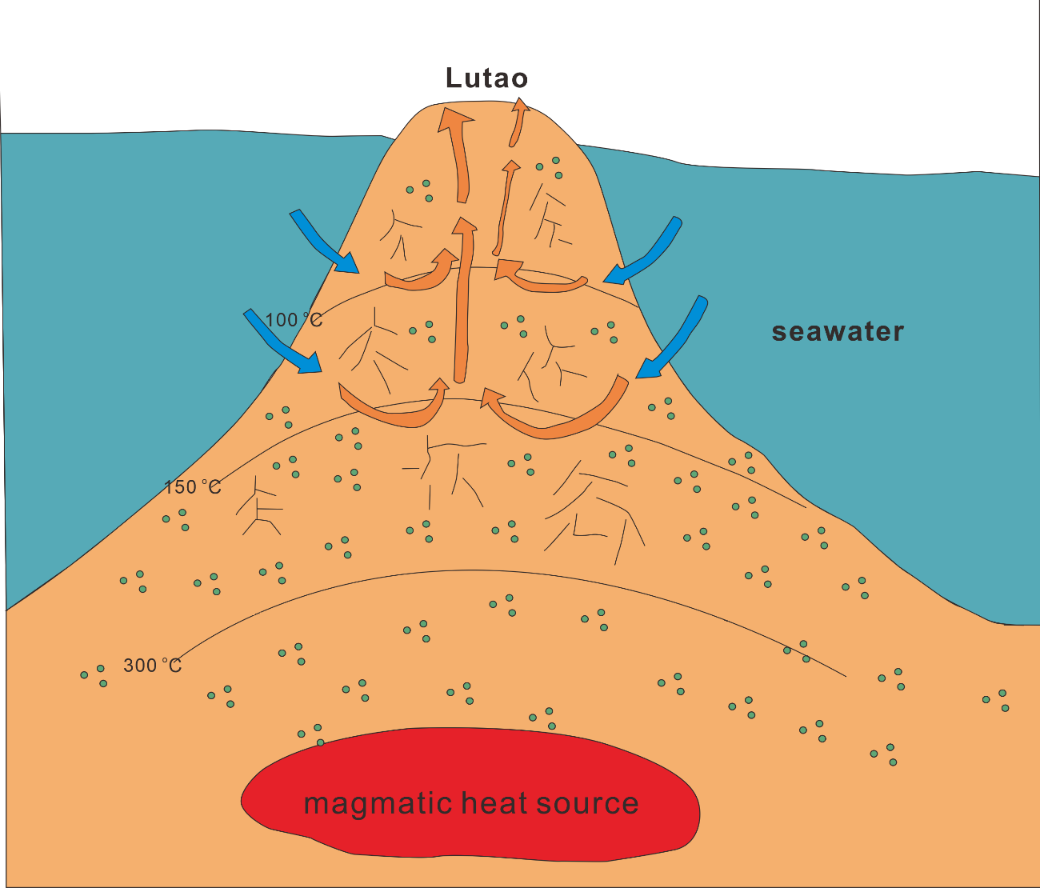


Fig. S6 Formation mechanism of Lutao methane: (upper figure) magmatic CO2 and H2O were trapped in the intrusive rock during Lutao volcanism at ~ 1.3 Ma. (bottom figure) These CO2-H2O rich inclusions achieved chemical and isotopic equilibrium with temperature gradients after long-term processing. Short-chain alkanes were formed from these inclusions via a one-step reaction (respeciation of CO2 and H2O buffered by Fe(II) minerals. H2 was not formed) or a two-step mechanism that combines serpentinization and Sabatier reaction/respeciation. These alkanes were leached by vent fluids during hydrothermal circulation.

# Fig. S7

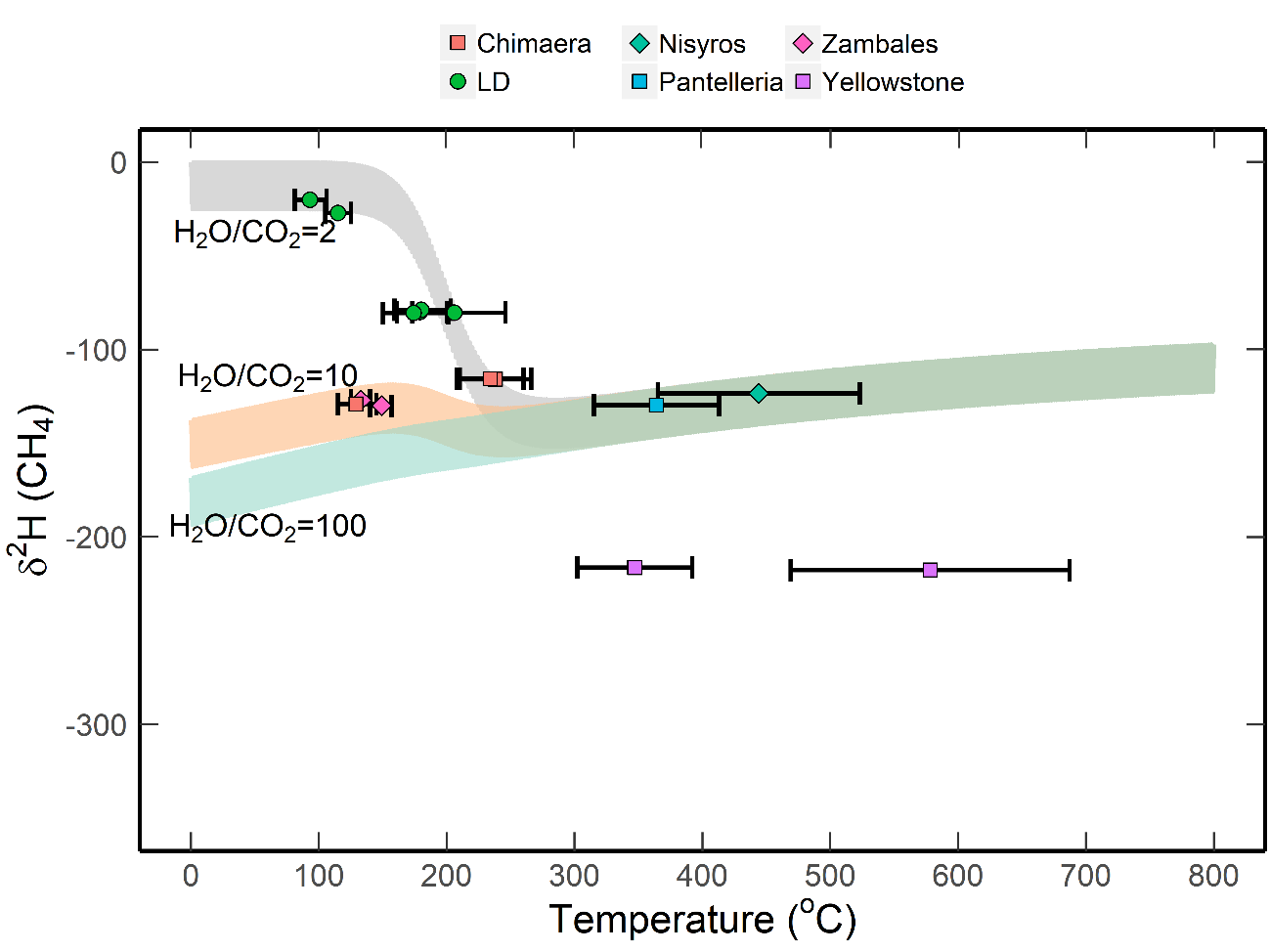


Fig. S7 Variations of δ2H values of methane (the gray area) as a function of equilibrium temperature in a closed system. The details on the D/H fractionation model are shown in the supporting information T3. Data source: Chimaera 22,23; LD (this study); Nisyros, Pantelleria, and Yellowstone 21; Zambales 47.

# Fig. S8

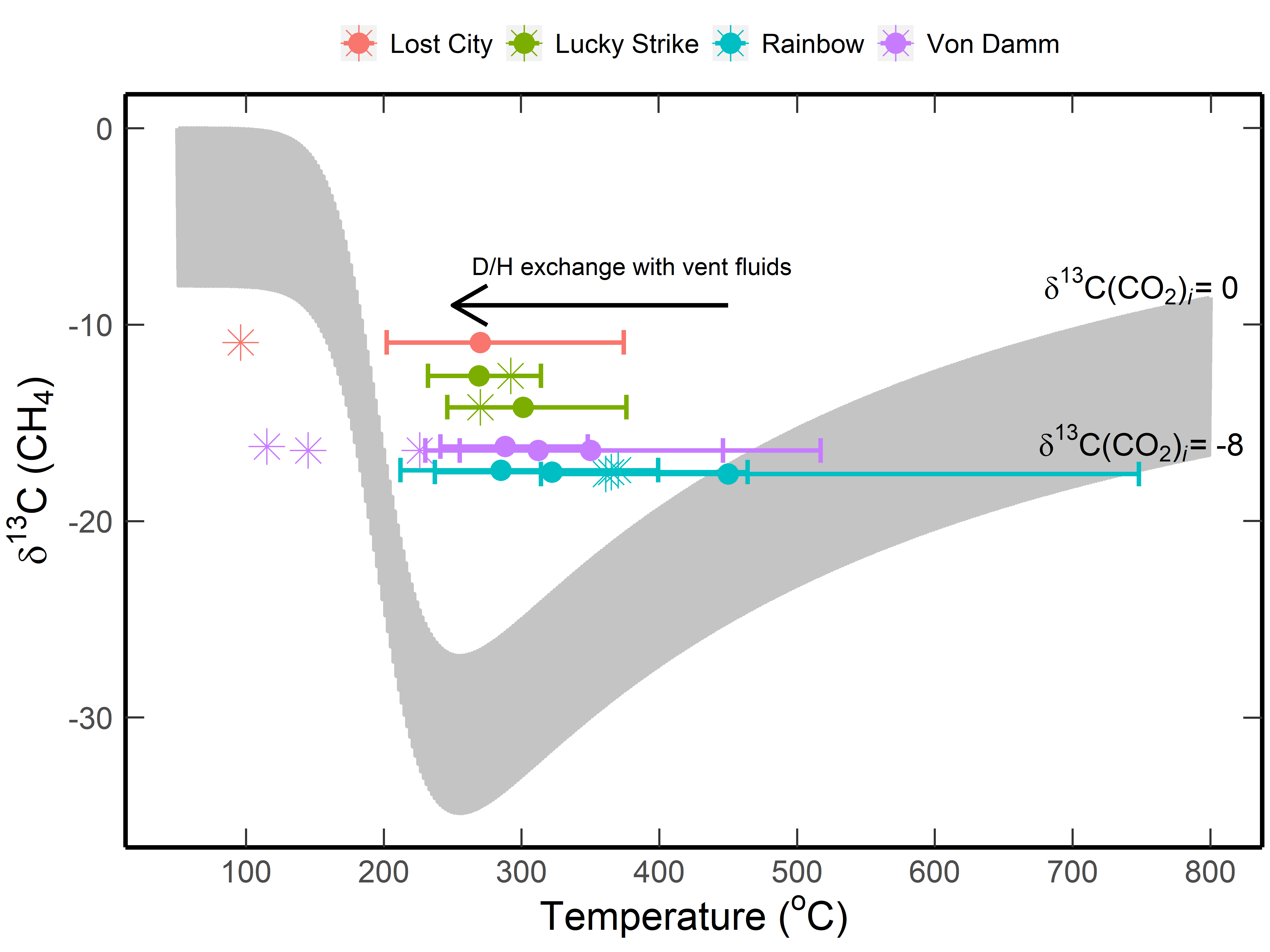


Fig. S8 Variation of equilibrium temperature and δ13C values of methane discharged from Mid-Ocean Ridge (MOR) hydrothermal system (Rainbow, Von Damm, Lost City, and Lucky Strike) 48. Temperatures were calculated from methane isotopologue (∆13CH3D) abundances. The gray area shows the estimated equilibrium δ13C(CH4) values in closed systems (Fig. 3). The vent temperatures are shown in asterisks. The fast D/H exchange between equilibrated CH4 and vent fluids decreased the apparent temperatures that calculated from the ∆13CH3D abundances.

# Table S1

Table S1. The chemical compositions of gas discharges from the Lutao ZDQ brine vent. Units: He, μmol/mol; all other components, mmol/mol.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Date | Sample | HgCl2 added | H2 | N2 | O2 | Ar | CO2 | He | *R/Ra* | *Rc/Ra* | 4He/20Ne |
| 2012/5/5 | 012a1 | No | n.d. | 805.8 | 60.9 | 4.7 | 1.1 | 237 | n.d. |  | 32.6 |
| 2014/4/29 | 014a1 | No | n.d. | 823.7 | 5.3 | 2.6 | 0.6 | 650 | 6.57 |  | n.d. |
| 2014/4/29 | 014a2 | No | n.d. | 816.1 | 60.3 | 4.4 | 1.1 | 370 | 6.67 |  | n.d. |
| 2014/4/30 | 014a3 | No | n.d. | 820.7 | 15.5 | 2.9 | 0.85 | 510 | 7.00 |  | n.d. |
| 2014/9/22 | 014b1 | No | n.d. | 823.3 | 9.9 | 3.0 | 4.2 | 234 | 4.97 | 4.99 | 76.8 |
| 2014/9/22 | 014b3 | No | n.d. | 837.2 | 27.4 | 5.4 | 19.8 | 161 | 5.56 | 5.60 | 30.6 |
| 2014/9/22 | 014b4 | No | n.d. | 815.4 | 44.8 | 4.2 | 7.4 | 170 | 5.10 | 5.14 | 34.7 |
| 2014/9/22 | 014b5 | No | n.d. | 820.4 | 20.6 | 3.5 | 9.2 | 185 | 4.90 | 4.93 | 52.7 |
| 2014/9/23 | 014b6 | No | n.d. | 828.4 | 61.7 | 6.2 | 22.2 | n.d. | 4.97 | 5.08 | 11.1 |
| 2014/9/23 | 014b7 | No | n.d. | 806.5 | 102.5 | 6.1 | 11.1 | n.d. | 4.25 | 4.39 | 7.5 |
| 2016/5/20 | 016z1 | Yes | b.d.l | 821.9 | 3.1 | 2.4 | 0.17 | 473 | 6.08 | 6.09 | 729.3 |
| 2016/5/20 | 016z3 | Yes | b.d.l | 822.1 | 3.2 | 2.4 | 0.51 | 501 | 6.26 | 6.26 | 715.7 |
| 2016/5/20 | 016z4 | Yes | b.d.l | 822.4 | 4.1 | 2.5 | 0.27 | 453 | 6.21 | 6.22 | 546.4 |
| 2016/5/21 | 016z5 | Yes | b.d.l | 822.0 | 1.8 | 2.4 | 0.22 | 473 | 5.93 | 5.94 | 151.0 |
| 2016/5/21 | 016z6 | No | b.d.l | 822.7 | 1.2 | 2.4 | 0.07 | 501 | 5.91 | 5.92 | 155.9 |
| 2016/5/21 | 016z7 | Yes | b.d.l | 820.0 | 16.1 | 2.9 | 0.14 | 465 | 5.97 | 5.99 | 66.2 |
| 2016/5/21 | 016z8 | Yes | b.d.l | 819.5 | 3.8 | 2.4 | 0.08 | 506 | 6.13 | 6.14 | 110.1 |
| 2016/5/22 | 016z9 | Yes | b.d.l | 821.2 | 7.7 | 2.6 | 0.21 | 500 | 5.76 | 5.77 | 679.6 |
| 2016/5/22 | 016z10 | No | b.d.l | 822.5 | 3.1 | 2.5 | 0.20 | 515 | 5.91 | 5.91 | 685.7 |
| 2016/5/22 | 016z11 | Yes | 0.99 | 806.8 | 90.2 | 5.3 | 0.13 | 310 | 5.94 | 5.97 | 42.5 |

Precision: ±3%.

*Rc/Ra* ratios were calculated from the *R/Ra* and 4He/20Ne ratios assuming that all 20Ne was originated from air contamination 43.

n.d. = not determined. b.d.l.= below detection limit.

# Table S2

Table S2. The chemical compositions of Lutao ZDQ hydrocarbons. Units: C1-C3, mmol/mol; C4 and C5, μmol/mol

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Date | Sample | CH4 | C2H6 | C3H8 | *i*-C4H10 | *n*-C4H10 | C5H12 |
| 2012/5/5 | 012a1 | 126.9 | 0.5 | 0.1 | n.d. | n.d. | n.d. |
| 2014/4/29 | 014a1 | 166.1 | 0.82 | 0.15 | n.d. | n.d. | n.d. |
| 2014/4/29 | 014a2 | 117.3 | 0.58 | 0.11 | n.d. | n.d. | n.d. |
| 2014/4/30 | 014a3 | 158.6 | 0.80 | 0.16 | n.d. | n.d. | n.d. |
| 2014/9/22 | 014b1 | 158.6 | 0.733 | 0.085 | n.d. | n.d. | n.d. |
| 2014/9/22 | 014b3 | 109.5 | 0.494 | 0.062 | n.d. | n.d. | n.d. |
| 2014/9/22 | 014b4 | 127.4 | 0.605 | 0.066 | n.d. | n.d. | n.d. |
| 2014/9/22 | 014b5 | 145.4 | 0.670 | 0.066 | n.d. | n.d. | n.d. |
| 2014/9/23 | 014b6 | 81.1 | 0.408 | 0.062 | n.d. | n.d. | n.d. |
| 2014/9/23 | 014b7 | 73.3 | 0.414 | 0.064 | n.d. | n.d. | n.d. |
| 2016/5/20 | 016z1 | 140.2 | 0.570 | 0.119 | 4.6 | 11.6 | 0.7 |
| 2016/5/20 | 016z3 | 170.7 | 0.569 | 0.116 | 5.4 | 11.9 | 1.6 |
| 2016/5/20 | 016z4 | 158.3 | 0.568 | 0.111 | 4.9 | 11.5 | 0.7 |
| 2016/5/21 | 016z5 | 156.4 | 0.553 | 0.114 | 4.9 | 10.8 | 1.0 |
| 2016/5/21 | 016z6 | 155.7 | 0.559 | 0.115 | 4.4 | 10.8 | 1.0 |
| 2016/5/21 | 016z7 | 142.6 | 0.658 | 0.131 | 5.9 | 13.2 | 1.4 |
| 2016/5/21 | 016z8 | 148.3 | 0.688 | 0.137 | 6.0 | 14.0 | 1.3 |
| 2016/5/22 | 016z9 | 112.4 | 0.710 | 0.145 | 6.2 | 14.3 | 1.4 |
| 2016/5/22 | 016z10 | 168.7 | 0.572 | 0.112 | 4.6 | 11.6 | 0.7 |
| 2016/5/22 | 016z11 | 32.5 | 0.124 | 0.024 | 1.2 | 2.3 | b.d.l. |

n.d. = not determined. b.d.l.= below detection limit.

Measurement uncertainties: samples collected in 2012 and 2014, ±5%; 2016 samples, ±2-10%

# Table S3

Table S3. The chemical and isotopic compositions of gas samples collected from the HWC vapor spring.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Date | sample | H2 | N2 | O2 | Ar | CO2 | CH4 | C2H6 | C3H8 | δ13C-C1 | δ13C-CO2 | δ13C-C2 | δ13C-C3 | δ2H-C1 | δ2H-C2 | δ2H-C3 |
| 2012/5/5 | 012a2 | n.d. | 899.5 | 0.4 | 3.0 | 7.9 | 88.9 | 0.2 | 0.1 | -10.7 | -18.5 | -13.4 | n.d. | n.d. | n.d. | n.d. |
| 2014/4/29 | 014w1 | n.d. | 910.0 | 35.4 | 4.0 | 2.9 | 47.1 | 0.09 | 0.04 | -8.1 | -16.6 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2014/4/30 | 014w2 | n.d. | 915.6 | 27.6 | 3.8 | 3.4 | 49.1 | 0.08 | 0.04 | -7.5 | -13.3 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2014/9/22 | 014s2 | n.d. | 875.9 | 82.4 | 5.8 | 3.8 | 31.9 | 0.066 | 0.040 | -12.9 | -12.9 | n.d. | n.d. | -117 | n.d. | n.d. |
| 2014/9/22 | 014s3 | n.d. | 841.4 | 132.8 | 7.9 | 3.1 | 14.6 | 0.045 | 0.020 | -10.5 | -13.2 | n.d. | n.d. | -55 | n.d. | n.d. |
| 2014/9/22 | 014s4 | n.d. | 919.3 | 20.3 | 4.1 | 9.1 | 46.9 | 0.062 | 0.113 | -7.1 | -14.6 | -15.1 | n.d. | 33 | n.d. | n.d. |
| 2014/9/23 | 014s6 | n.d. | 927.3 | 12.8 | 3.9 | 5.8 | 49.8 | 0.113 | 0.053 | -9.9 | -17.2 | n.d. | n.d. | 34 | n.d. | n.d. |
| 2014/9/23 | 014s8 | n.d. | 881.5 | 63.0 | 5.5 | 16.3 | 33.4 | 0.060 | 0.045 | -9.5 | -14.3 | n.d. | n.d. | 41 | n.d. | n.d. |
| 2016/5/20 | 016w1 | n.d. | 939.9 | 5.3 | 3.3 | 3.6 | 50.1 | 0.036 | 0.035 | -6.3 | -12.2 | -11.2 | -37.9 | 17 | -141 | -179 |
| 2016/5/20 | 016w2 | n.d. | 940.9 | 6.0 | 3.3 | 2.4 | 51.1 | 0.036 | 0.029 | -6.0 | -8.4 | -7.8 | -31.2 | 18 | -135 | -178 |
| 2016/5/20 | 016w3 | 5.88 | 931.0 | 8.6 | 3.2 | 3.1 | 49.0 | 0.042 | 0.029 | -6.7 | -10.5 | -11.2 | -27.5 | 14 | -146 | n.d. |
| 2016/5/20 | 016w4 | 4.12 | 935.3 | 7.0 | 3.3 | 2.2 | 48.0 | 0.037 | 0.028 | -7.2 | -8.6 | -8.6 | -26.4 | n.d. | n.d. | n.d. |
| 2016/5/21 | 016w5 | 3.75 | 936.8 | 3.8 | 3.3 | 4.0 | 46.5 | 0.033 | 0.026 | -6.5 | -11.7 | -8.2 | -21.4 | n.d. | n.d. | n.d. |
| 2016/5/21 | 016w6 | n.d. | 942.7 | 2.7 | 3.3 | 2.9 | 47.1 | 0.034 | 0.028 | -6.6 | -12.4 | -9.2 | -21.8 | n.d. | n.d. | n.d. |
| 2016/5/21 | 016w7 | 5.32 | 934.6 | 4.3 | 3.2 | 3.6 | 47.1 | 0.041 | 0.030 | -7.2 | -12.1 | -10.8 | -13.0 | 11 | -115 | n.d. |
| 2016/5/21 | 016w8 | n.d. | 932.6 | 15.8 | 3.6 | 2.4 | 43.2 | 0.033 | 0.028 | -6.8 | -12.5 | -8.4 | -12.9 | 11 | -114 | n.d. |
| 2016/5/22 | 016w9 | 1.53 | 938.8 | 2.6 | 3.3 | 4.3 | 46.5 | 0.035 | 0.027 | -6.2 | -13.3 | -7.6 | -13.0 | 10 | -130 | n.d. |
| 2016/5/22 | 016w10 | n.d. | 932.6 | 14.3 | 3.7 | 3.7 | 43.3 | 0.030 | 0.026 | -6.4 | -14.2 | -6.3 | -13.6 | n.d. | n.d. | n.d. |
| 2016/5/22 | 016w11 | n.d. | 939.2 | 5.6 | 3.3 | 3.6 | 47.0 | 0.035 | 0.027 | -7.1 | -14.8 | -6.3 | -13.0 | n.d. | n.d. | n.d. |
| 2018/10/30 | 018WG3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | -10.5 | n.d. | n.d. | n.d. | -27 | n.d. | n.d. |
| 2018/10/30 | 018WG4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | -10.2 | n.d. | n.d. | n.d. | -20 | n.d. | n.d. |

\* The units and measurement uncertainties are identical to those listed in Table 1, Table S1 and S2.

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