

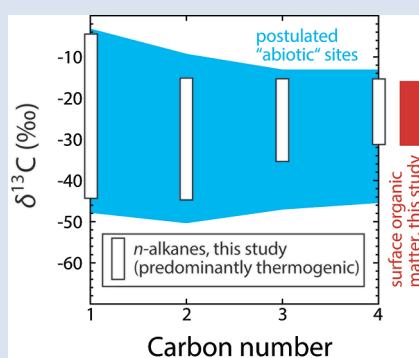
Abiogenesis not required to explain the origin of volcanic-hydrothermal hydrocarbons

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Abstract



of abiogenesis. Further considering the ubiquitous presence of surface waters in Earth's crust, abiotic hydrocarbon occurrences might have been significantly overestimated.

Abiotic formation of *n*-alkane hydrocarbons has been postulated to occur within Earth's crust. Apparent evidence was primarily based on uncommon carbon and hydrogen isotope distribution patterns that set methane and its higher chain homologues apart from biotic isotopic compositions associated with microbial production and closed system thermal degradation of organic matter. Here, we present the first global investigation of the carbon and hydrogen isotopic compositions of *n*-alkanes in volcanic-hydrothermal fluids hosted by basaltic, andesitic, trachytic and rhyolitic rocks. We show that the bulk isotopic compositions of these gases follow trends that are characteristic of high temperature, open system degradation of organic matter. In sediment-free systems, organic matter is supplied by surface waters (seawater, meteoric water) circulating through the reservoir rocks. Our data set strongly implies that thermal degradation of organic matter is able to satisfy isotopic criteria previously classified as being indicative

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Introduction

The ability to distinguish between biotic and abiotic hydrocarbon sources on Earth is essential to understand fully the formation of crustal hydrocarbon reservoirs, identify the origin of hydrocarbons such as methane on other planets and resolve the potential role of abiotic methane in the emergence of life. It is well known that crustal hydrocarbons largely derive from biotic sources, *i.e.* from microbial production and thermal decomposition of organic matter (*e.g.*, Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014). Abiotic hydrocarbon formation (*i.e.* generation from pure inorganic substances, without any involvement of organic carbon) has been postulated to take place in a variety of natural systems where inorganically derived CO or CO₂, water, reducing reagents and catalysts and/or heat are available. These include hydrothermal and low temperature (*T* < 100 °C) mafic and ultramafic systems, subduction-related, volcanic-hydrothermal systems and igneous intrusions (*e.g.*, Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014).

Most prominently, the following criteria have been used to identify abiotic hydrocarbon occurrences: i) methane with $\delta^{13}\text{C} \geq -20\text{‰}$ (*e.g.*, Welhan and Craig, 1979), ii) the occurrence of a carbon isotope reversal between ethane and methane (*i.e.* methane more enriched in ¹³C than ethane, contrary to what is observed for *n*-alkanes from confined sedimentary hydrocarbon reservoirs) (*e.g.*, Des Marais *et al.*, 1981; Sherwood Lollar *et al.*, 2002; Proskurowski *et al.*, 2008) and iii) methane in apparent chemical and isotopic equilibrium with inorganically derived CO₂ (Fiebig *et al.*, 2007). Using these criteria, contrary views have been presented on the origin of volcanic-hydrothermal *n*-alkanes. Whereas Des Marais *et al.* (1981) identified Yellowstone hydrocarbons to derive from a thermogenic source, Fiebig *et al.* (2007) ascribed *n*-alkanes from Nisyros, Vesuvio and Ischia to an abiotic origin. Recently, ¹³C-labelled experiments have called the relevance of abiotic hydrocarbon production under hydrothermal conditions into question, due to sluggish reaction rates (McCollom, 2016). Here, we present and discuss the first global data set of the carbon and hydrogen

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isotope compositions of *n*-alkanes in hydrothermal fluids to gain more detailed insights into hydrocarbon formation under natural hydrothermal conditions.

Methods

We sampled two phase well fluids ($n = 29$) and steam vent fumaroles ($n = 61$) from 28 volcanic-hydrothermal fields in New Zealand, Iceland, Argentina, USA (Alaska), Italy, Greece, Portugal (Azores) and Spain (Canary Islands) (Table S-1). Sampled locations represent all types of volcanism and a wide range of reservoir temperatures (200 – 450 °C), with the origin of external water being dominantly meteoric and/or seawater (Table S-1 and references therein). Terrestrial vegetation at the sampled sites is largely dominated by C_3 plants (Still *et al.*, 2003). We analysed the carbon isotopic compositions of methane, ethane, propane and *n*-butane as well as the hydrogen isotopic compositions of methane and water in the discharged fluids (Supplementary Information; Tables S-2, S-3).

Results and Discussion

For several locations, carbon isotopes are homogeneously distributed among ethane, propane and *n*-butane (C_{2+} hydrocarbons), with variations in $\delta^{13}C_{C_{2+}} \leq 1.0$ ‰ (Fig. 1a). At Reykjanes, $\delta^{13}C_{C_{2+}}$ of –16 ‰ (well 11) and –17 to –18 ‰ (well 12) overlap with the carbon isotopic composition of particulate organic carbon (-17.5 ‰ $\geq \delta^{13}C_{POC} \geq -22.2$ ‰) and modern sedimentary organic matter (-16.5 ‰ $\geq \delta^{13}C_{SOM} \geq -19.4$ ‰) that are characteristic of the water masses surrounding the Reykjanes peninsula (Sara *et al.*, 2007). For Esguicho (Furnas village) $\delta^{13}C_{C_{2+}}$ of –28 to –29 ‰ perfectly agree with the average carbon isotopic composition of terrestrial plants growing in the Furnas caldera (–28.4 ‰; Pasquier-Cardin *et al.*, 1999). The hydrothermal reservoir at Reykjanes is predominantly fed by seawater, whereas the hydrothermal system beneath Furnas village is exclusively sourced by meteoric water (Table S-1). The same patterns - invariant $\delta^{13}C_{C_{2+}}$, but absolute values changing with the source of water - are observed at Nisyros (seawater-fed hydrothermal system, $\delta^{13}C_{C_{2+}}$ around –18 ‰), Ischia and Rotokawa well 14 (both meteoric water-fed systems, $\delta^{13}C_{C_{2+}}$ around –27 ‰) (Fig. 1a; Table S-1). These observations strongly imply that local organic matter is transported by external waters into the corresponding hydrothermal reservoirs, where it is finally subjected to high temperature pyrolysis. At these temperatures, the carbon isotope fractionation between the C_{2+} hydrocarbons and the source organic matter becomes insignificantly small and, hence, the $\delta^{13}C_{C_{2+}}$ becomes indicative of the bulk organic matter decomposing at depth.

Thermogenic C_{2+} hydrocarbon production is not restricted to systems with invariant $\delta^{13}C_{C_{2+}}$, but is most likely important in all systems. Although the majority of sampled discharges exhibit significant differences among $\delta^{13}C_{C_{2+}}$ values (Tables S-2, S-3), the carbon isotopic composition of *n*-butane, the longest *n*-alkane analysed in this study, consistently occurs within the range reported for modern marine dissolved organic carbon (-18 ‰ $\geq \delta^{13}C_{DOC} \geq -23$ ‰; Druffel *et al.*, 1992), modern marine particulate organic carbon (-17 ‰ $\geq \delta^{13}C_{POC} \geq -25$ ‰; Druffel *et al.*, 1992; Sara *et al.*, 2007) and modern terrestrial C_3 plants (-20 ‰ $\geq \delta^{13}C \geq -37$ ‰, with most data clustering between -23 ‰ $\geq \delta^{13}C \geq -31.5$ ‰ and averaging at $\delta^{13}C = -28.5$ ‰; Kohn, 2010) (Fig. 1b). Moreover, relative variations in $\delta^{13}C$ decrease in the order ethane – propane – *n*-butane (Fig. 1b). Both patterns are consistent with isotope fractionation principles of organic matter degradation according to which the carbon isotope fractionation between

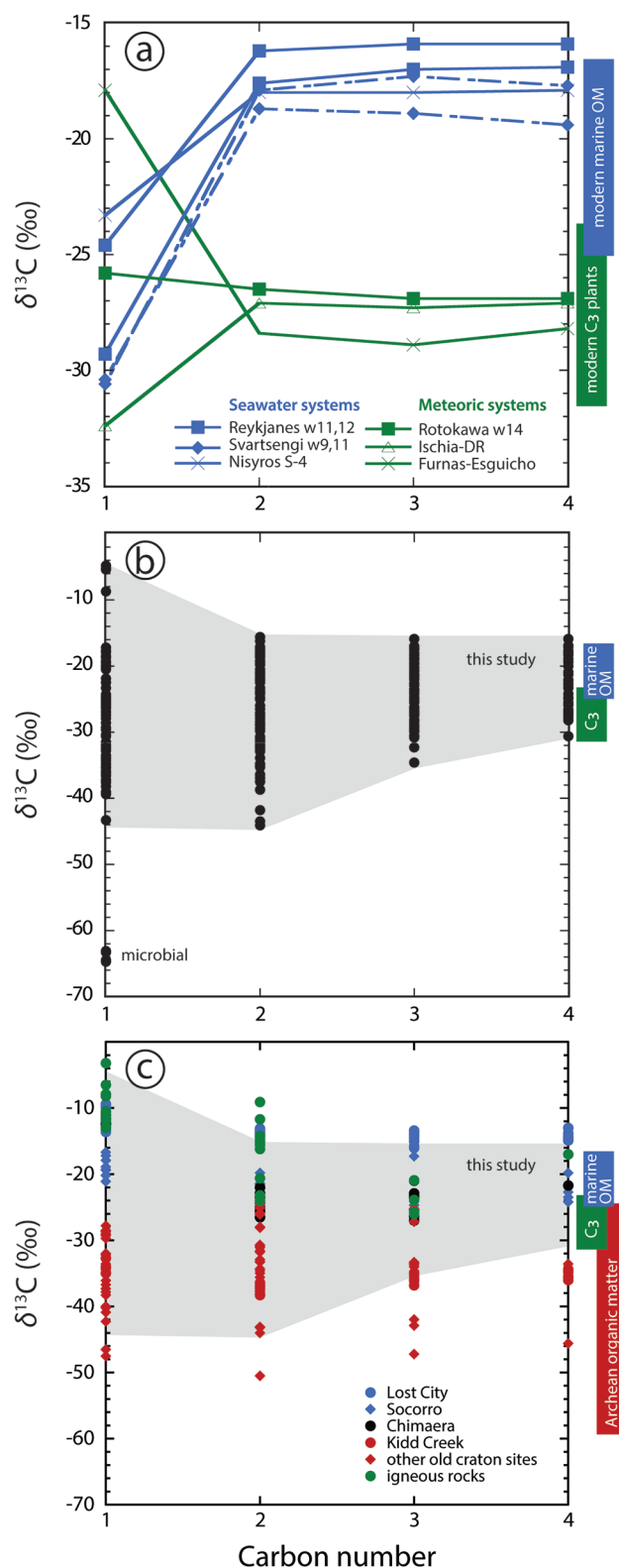


Figure 1 Plot of $\delta^{13}C$ of individual *n*-alkanes against carbon number. $\delta^{13}C$ ranges of modern marine organic matter (Druffel *et al.*, 1992; Sara *et al.*, 2007), terrestrial C_3 vegetation (Kohn, 2010) and Archean organic matter (Hayes and Waldbauer, 2006) are shown for comparison. (a) Emissions that are characterised by invariant $\delta^{13}C_{C_{2+}}$. (b) Compilation of all *n*-alkane data analysed in this study. (c) Comparison between *n*-alkane data from this study (area in grey) and data available from abiotic sites (Supplementary Information): hydrothermal sites (blue); ophiolite gases (black); old craton gases (red) and inclusions in igneous rocks (green).

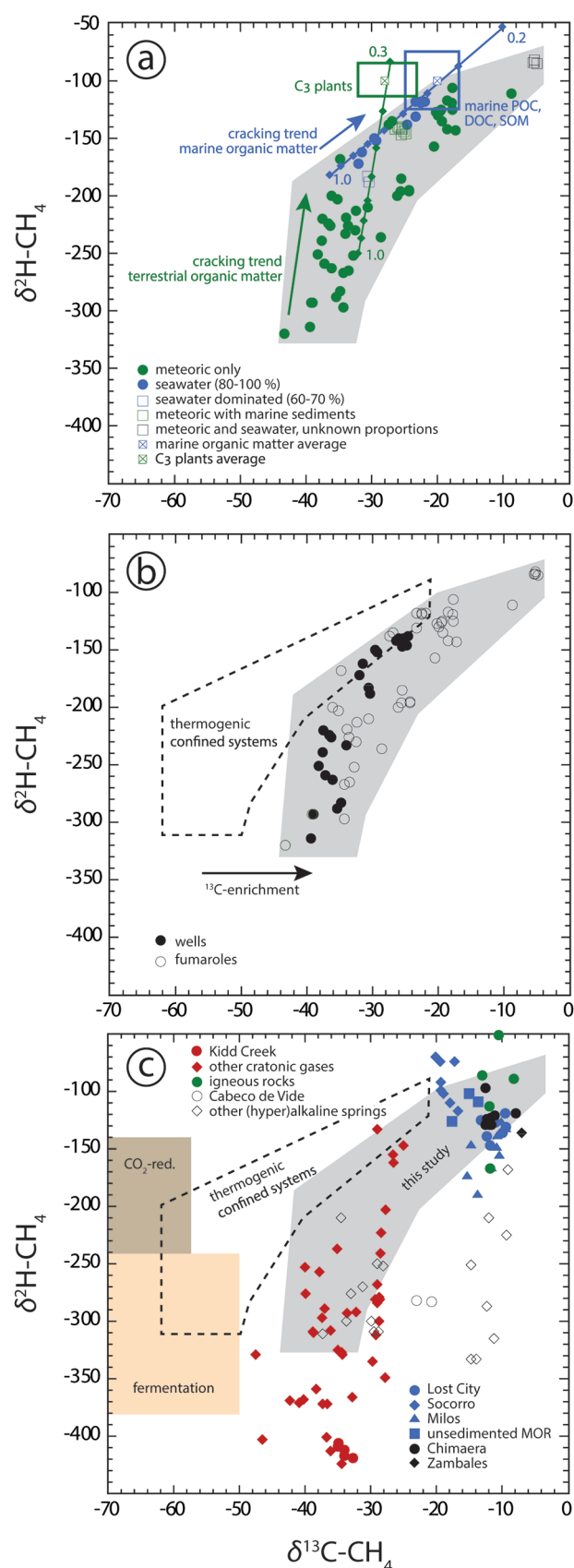


Figure 2 Plot of $\delta^2\text{H-CH}_4$ vs. $\delta^{13}\text{C-CH}_4$. Samples with an obvious microbial origin ($\delta^{13}\text{C-CH}_4 < -60$ ‰, Fig. 1b) are not considered. (a) Data classified after the origin of external water feeding the hydrothermal system (Table S-1). Blue and green squares are representative of the carbon and hydrogen isotopic compositions of marine organic matter and C₃ plants, respectively (Schoell, 1984). The carbon and hydrogen isotopic compositions of instantaneously generated fractions of methane deriving from open

system cracking of marine and terrestrial (C₃ plants) organic matter were modelled as a function of the fraction of precursor sites remaining inside the cracked organic matter (Supplementary Information). The cracking trend for methane deriving from marine organic matter (blue line) matches the variation of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ observed for seawater-fed hydrothermal systems (blue data points). The cracking trend for methane from terrestrial organic matter (green line) corresponds to the slope described by most low $\delta^{13}\text{C-CH}_4$ samples from meteoric water-fed hydrothermal systems (green data points), but – on average – occurs shifted relative to the latter to higher $\delta^{13}\text{C}$ and $\delta^2\text{H}$. This implies that methane precursor sites in decomposing terrestrial organic matter either occur depleted in ^{13}C and ^2H with respect to the average C₃ plant isotopic composition or that the corresponding carbon and hydrogen isotope fractionations (α_C , α_H) are larger than those obtained from xylite (Berner *et al.*, 1995), with α_H/α_C remaining unchanged. Both possibilities are consistent with carbon isotope constraints on pyrolysis of coal (Cramer *et al.*, 1998). (b) Data classified after the style of degassing (wells vs. fumaroles). (c) Comparison between methane data from this study and data available from other abiotic sites (Supplementary Information): labelling as in Figure 1c, extended by (hyper)alkaline spring data (open symbols). Field characteristic for methane from microbial (c) and confined sedimentary systems (b, c) redrawn after Schoell (1988).

source organic matter and the evolving gaseous *n*-alkane decreases with the number of carbon atoms constituting the *n*-alkane (Tang *et al.*, 2000). In addition to the modern organic matter supplied by external waters, older organic matter contained in sediments can also contribute to overall hydrocarbon production, as becomes evident from Rotokawa $\delta^{13}\text{C-C}_{2+}$ data (Table S-2). Although the Rotokawa hydrothermal reservoir is exclusively sourced by meteoric waters (Table S-1), its $\delta^{13}\text{C-n-C}_4$ values range from -27 to -17 ‰, pointing to the occurrence of a marine next to a terrestrial organic source. The marine organic end member is likely hosted in Mesozoic greywacke located at relatively shallow depths of 1–3 km underneath Rotokawa (Table S-1 and references therein).

Several additional observations imply that methane in the sampled discharges is also predominantly derived from the thermal decomposition of organic matter, and that the source organics are transported by external waters from the surface to reservoir depth. First, even if methane samples with an obvious microbial origin (Furnas B and Furnas Lake 2, Azores; Table S-3), as indicated by relatively strong depletions in ^{13}C and ^2H ; Whiticar *et al.*, 1999) are excluded, methane still exhibits the largest variations in $\delta^{13}\text{C}$ of all analysed *n*-alkanes (Fig. 1b). Second, in $\delta^{13}\text{C}$ vs. $\delta^2\text{H}$ space (Fig. 2a), methane from meteoric water- and seawater-fed hydrothermal systems plots along trends that are characteristic of open system, high temperature cracking of terrestrial and marine organic matter, respectively (Berner *et al.*, 1995; Supplementary Information). Third, in the same space, methane from volcanic-hydrothermal systems plots into a field that has a shape similar to that characteristic of thermogenic methane from confined sedimentary systems but is, relative to the latter, shifted to higher $\delta^{13}\text{C}$ values (Fig. 2b). Generally, the magnitude of carbon isotope fractionation between precursor organic matter and evolving *n*-alkane decreases with increasing temperature (e.g., Tang *et al.*, 2000). The observed ^{13}C -enrichment of thermogenic methane in volcanic-hydrothermal fluids may, therefore, result from relatively high reservoir temperatures of 200 – 450 °C (Table S-1), well-exceeding those of confined sedimentary reservoirs where methane generation takes place primarily between ~ 150 – 220 °C (Quigley and MacKenzie, 1988). In addition, modern marine organic matter is enriched in ^{13}C by 5 to 10 ‰ relative to the marine organic matter of pre-Cenozoic age (Hayes *et al.*, 1999) that provides the source of kerogen in confined sedimentary reservoirs. Fourth, in Icelandic systems, which are characterised by the absence of

organic sediments, DOC and POC concentrations of meteoric water and/or seawater alone are sufficiently high to balance *n*-alkane concentrations in the discharged fluids (Fig. S-1). Fifth, under steady state conditions, water recharge rates at depth should be higher in well reservoirs than in naturally degassing systems, as in well systems the reservoir fluid is continuously exploited at the surface in addition to the steam. The flux of fresh, immature organics (depleted in ^{13}C) through the reservoir should, therefore, be higher in well systems. This is consistent with the observation that well discharges display on average lower $\delta^{13}\text{C}\text{-CH}_4$ values than fumaroles (Fig. 2b).

Two reasons may account for $\delta^2\text{H}$ departing from the predicted cracking and degassing trends at high organic matter maturities characterised by $\delta^{13}\text{C}\text{-CH}_4 \geq -20\text{‰}$ (Fig. 2a). First, hydrogen isotope exchange between CH_4 and water may occur at the elevated temperatures characteristic of hydrothermal systems, driving CH_4 towards isotopic equilibrium with water at $T \geq 300\text{ °C}$ (Fig. S-2a). Alternatively, the decomposing organic matter at depth may be able to exchange hydrogen with the reservoir water such that the hydrogen isotopic composition of the organic matter and that of the methane becomes progressively buffered by water with increasing temperature and/or increasing organic matter maturity.

The isotopic signature of *n*-alkanes from potential abiotic natural sites and our samples are shown for comparison in Figs. 1c and 2c. There is significant overlap between our data and the inferred abiotic data set. However, based on our observations we consider a predominantly abiotic origin for the volcanic-hydrothermal hydrocarbons to be highly unlikely. In particular, a predominantly abiotic origin of the *n*-alkanes analysed in this study would require that our overall data set fortuitously follows isotopic fractionation principles that are characteristic of thermogenesis as detailed above.

Our observation that the overall isotopic trends displayed by volcanic-hydrothermal hydrocarbons are consistent with a predominant thermogenic origin for these gases has important implications for the reliability of criteria previously applied to identify abiotic hydrocarbon occurrences. First, $\delta^{13}\text{C}\text{-CH}_4$ values exceeding those characteristic for methane from confined sedimentary systems are not indicative of abiogenesis (Fig. 2a). Second, the occurrence of a carbon isotope reversal (as is observed for several locations in this study; see Tables S-2, S-3) cannot be used as evidence for abiotic *n*-alkane generation either. Reversals can be obtained from thermogenic degradation and open system degassing alone (Fig. S-3), or from mixing of thermogenic *n*-alkanes from two or more sources of distinct organic maturity (Taran *et al.*, 2007). Third, because $\delta^{13}\text{C}\text{-CH}_4$ is controlled by the relative fluxes of organic carbon into and methane carbon out of the system, carbon isotope equilibrium between CH_4 and CO_2 might not be attained, such that the apparent fractionation would only fortuitously correspond to equilibrium in some cases (Figs. S-2b, S-4).

Conclusions

$\delta^2\text{H}$ and $\delta^{13}\text{C}$ of CH_4 as well as $\delta^{13}\text{C}$ of C_{2+} of *n*-alkanes from volcanic-hydrothermal emissions follow isotopic trends that are consistent with the principles of organic matter degradation under relatively high temperatures and open system conditions. No significant contribution from an abiotic source is required to explain the isotopic compositions and trends displayed by these *n*-alkanes. Source organic matter is supplied by external, surface-derived waters circulating through these systems and, if present, by sedimentary host rocks. Previously applied criteria characteristic for thermogenic hydrocarbon classification were developed for confined sedimentary

thermogenic systems such as oil and gas fields that were not open to degassing during organic matter maturation. We argue that these criteria are not applicable to thermogenic systems open to degassing. Under such open system conditions, unusual enrichment in ^{13}C and even carbon isotope reversals between methane and ethane can be obtained. As a consequence, reported abiotic hydrocarbon occurrences may be significantly overestimated, by mistakenly ascribing thermogenic hydrocarbons to an abiotic origin.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1920>.



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■ Supplementary Information

The Supplementary Information includes:

- 1. Methods
- 2. Sampled Locations
- 3. Data Modelling
- 4. Additional Data (Displayed in Figures)
- Tables S-1 to S-3
- Figures S-1 to S-4
- Supplementary Information References

1. Methods

Well fluids, well steam and natural gas discharges were sampled following standard protocols for fumaroles (Giggenbach, 1975; Cioni and Corazza, 1981) and bi-phase well discharges (Arnórsson *et al.* 2006). A variety of analytical setups was used to analyse the stable isotopic composition of *n*-alkanes, CO₂ and water. Carbon isotope analysis of *n*-alkanes and CO₂ were performed using analytical setups described by Fiebig *et al.* (2015). For hydrogen isotope analysis of CH₄, a sample preconcentration system was connected to a GC/TC (Thermo Finnigan), equipped with a Porapak Q column. CH₄ was separated from H₂ by keeping the column isothermal at –50 °C and finally introduced into a MAT 253 gas source mass spectrometer (Thermo Finnigan) using He as a carrier gas. The hydrogen isotopic composition of water was analysed using a TC-EA (Thermo Finnigan). Raw isotopic data were corrected analysing isotopic reference materials (whose known isotopic compositions bracket those of the samples) along with the samples, following the principle of identical treatment of sample and reference materials (*e.g.*, Meier-Augenstein and Schimmelmann, 2019). Methane#1, methane#3, ALM methane#7 (all supplied by A. Schimmelmann, Indiana University) and two inhouse CH₄ standards (calibrated against methane #1, #3 and #7) were used for the correction of raw $\delta^{13}\text{C}_{1-4}$ and raw $\delta^2\text{H-C}_1$, three inhouse CO₂ gases anchored on the VPDB-LSVEC for the correction of raw $\delta^{13}\text{CO}_2$, and three inhouse water samples calibrated on the VSMOW-SLAP scale for the correction of raw $\delta^2\text{D-H}_2\text{O}$. External precision for carbon isotope analysis was ± 0.5 ‰ for *n*-alkanes



and ± 0.2 ‰ for CO₂. External precisions for $\delta^2\text{H}$ analysis of CH₄ and H₂O were $\leq \pm 5$ ‰ and $\leq \pm 3$ ‰, respectively. All isotopic data are presented in Tables S-2 (wells) and S-3 (fumaroles).

2. Sampled Locations

Information about the major characteristics of each sampled site, with respect to tectonic setting, host rocks and the source of water feeding the corresponding hydrothermal system at depth is provided in Table S-1 (see references there for further reading). Tables S-2 and S-3 list the carbon and hydrogen isotopic compositions of *n*-alkanes in well discharges and fumaroles, respectively, as well as the hydrogen isotopic compositions of discharged water vapour and liquid water.

3. Data Modelling

3.1. Temperature dependence of the hydrogen isotope fractionation between H₂O_(v) and CH₄

For a given temperature between 200 °C and 400 °C (Figs. S-2, S-4), the hydrogen isotope fractionation between water vapour and methane ($\alpha_{\text{H}_2\text{O}-\text{CH}_4}$) can be computed from the hydrogen isotope fractionations between water vapour and H₂ ($\alpha_{\text{H}_2\text{O}-\text{H}_2}$) and CH₄ and H₂ ($\alpha_{\text{CH}_4-\text{H}_2}$) according to

$$\alpha_{\text{H}_2\text{O}-\text{CH}_4} = \alpha_{\text{H}_2\text{O}-\text{H}_2} / \alpha_{\text{CH}_4-\text{H}_2} \quad (\text{Eq. S-1})$$

Temperature dependencies for $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ were determined experimentally by Suess (1949) and theoretically by Bardo and Wolfsberg (1976), whereas the temperature dependence of $\alpha_{\text{CH}_4-\text{H}_2}$ was experimentally constrained by Horibe and Craig (1995). Note that values of +2 ‰, −6 ‰, −17 ‰, −30 ‰ and −39 ‰ must finally be added to values of $1000 \cdot \ln(\alpha_{\text{H}_2\text{O}-\text{CH}_4})$ at temperatures of 200 °C, 250 °C, 300 °C, 350 °C and 400 °C, respectively, to account for polymerisation of water vapour monomers at temperatures ≥ 200 °C (Driesner, 1997).

3.2. Modelling of open system cracking of organic matter

A variety of parameters controls the carbon and hydrogen isotopic composition of gaseous *n*-alkanes deriving from the thermal decomposition of organic matter. Amongst these are temperature, the initial isotopic composition of the parental organic matter, site specific isotope fractionations inside the parental organic matter (as each *n*-alkane can be derived from different precursor sites within), the degree of cracking and open *vs* closed system degassing (Clayton, 1991; Rooney *et al.*, 1995; Berner *et al.*, 1995; Lorant *et al.*, 1998). Both pyrolysis experiments and theoretical computations provided evidence that the apparent carbon isotope fractionation between a given precursor site in the organic matter and the evolving gaseous *n*-alkane decreases with the number of carbon atoms constituting the *n*-alkane and with temperature (Clayton, 1991; Berner *et al.*, 1995; Tang *et al.*, 2000). If site-specific isotope fractionations within the organic matter can be neglected, generated *n*-alkanes can, therefore, be expected to approach the carbon isotopic composition of the initial source material with increasing chain length and with increasing temperature (Chung *et al.*, 1988). Upon degassing, the different precursor sites inside the organic matter will, however, change their isotopic compositions differently, depending on the magnitude of isotope fractionation between a given *n*-alkane and its corresponding precursor site, the mode of gas generation (closed *vs*. open system) and the fraction of *n*-alkane generated (Clayton, 1991; Rooney *et al.*, 1995). For a given *n*-alkane precursor site, the effect of open system cracking on its bulk carbon isotopic composition can be modelled using equation (3) of Clayton (1991):

$$\delta^{13}\text{C}_{\text{PS}} = (1000 + \delta^{13}\text{C}_i) * f_{\text{PS}}^{(\alpha_{\text{C}} - 1)} - 1000 \quad (\text{Eq. S-2})$$

where $\delta^{13}\text{C}_{\text{PS}}$ is the carbon isotopic composition of the precursor site specific for a given *n*-alkane inside the organic matter, $\delta^{13}\text{C}_i$ the initial carbon isotopic composition of the specific precursor site, α_{C} the carbon isotope fractionation factor between a given *n*-alkane and its precursor site and f_{PS} the fraction of residual precursor sites. Further, it is

$$f_{\text{PS}} = 1 - f_{\text{n-alk}} \quad (\text{Eq. S-3})$$

and

$$\delta^{13}\text{C}_{\text{n-alk}} = \alpha_{\text{C}} * (1000 + \delta^{13}\text{C}_{\text{PS}}) - 1000 \quad (\text{Eq. S-4})$$



where $f_{n\text{-alk}}$ is the fraction of n -alkane generated and $\delta^{13}\text{C}_{n\text{-alk}}$ the carbon isotopic composition of the corresponding instantaneously generated fraction of n -alkane. Insertion of (Eq. S-2) and (Eq. S-3) in (Eq. S-4) yields

$$\delta^{13}\text{C}_{n\text{-alk}} = \alpha_{\text{C}} * (1000 + \delta^{13}\text{C}_{\text{I}}) * (1 - f_{n\text{-alk}})^{(\alpha_{\text{C}} - 1)} - 1000 \quad (\text{Eq. S-5})$$

3.2.1. Modelling the carbon isotopic compositions of instantaneously generated fractions of methane, ethane and propane. Equation S-5 can be used to model the evolution of the carbon isotopic composition of a given n -alkane as a function of the fraction of n -alkane generated (Figs. S-3a,b,c). See there for more specific details on α -values and $\delta^{13}\text{C}_{\text{I}}$ chosen for data modelling.

3.2.2. Modelling the carbon and hydrogen isotopic compositions of instantaneously generated fractions of methane. The carbon and hydrogen isotopic compositions of instantaneously generated fractions of methane have been modelled as a function of the fraction of residual precursor sites for open system cracking of both marine and terrestrial organic matter in Figure 2a. In analogy to Equation S-5, the following equations were used for this purpose:

$$\delta^{13}\text{C}_{\text{CH}_4} = \alpha_{\text{C}} * (1000 + \delta^{13}\text{C}_{(\text{CH}_4)\text{I}}) * f_{\text{PS}(\text{CH}_4)}^{(\alpha_{\text{C}} - 1)} - 1000 \quad (\text{Eq. S-6})$$

$$\delta^2\text{H}_{\text{CH}_4} = \alpha_{\text{H}} * (1000 + \delta^2\text{H}_{(\text{CH}_4)\text{I}}) * f_{\text{PS}(\text{CH}_4)}^{(\alpha_{\text{H}} - 1)} - 1000 \quad (\text{Eq. S-7})$$

For open system cracking of marine organic matter, α_{C} and α_{H} were set to 0.983 and 0.909, respectively (as constrained from pyrolysis experiments of marine kukersite; Berner *et al.* 1995), and the initial isotopic composition of methane precursor sites ($\delta^{13}\text{C}_{(\text{CH}_4)\text{I}}$, $\delta^2\text{H}_{(\text{CH}_4)\text{I}}$) was assumed to be identical to the average isotopic composition of marine organic matter ($\delta^{13}\text{C} = -20$ ‰, $\delta^2\text{H} = -100$ ‰; Schoell, 1984). For open system cracking of terrestrial organic matter, α_{C} and α_{H} were set to 0.9958 and 0.8333, respectively (as constrained from pyrolysis experiments of terrestrial xylite, Berner *et al.*, 1995), and the initial isotopic composition of methane precursor sites ($\delta^{13}\text{C}_{(\text{CH}_4)\text{I}}$, $\delta^2\text{H}_{(\text{CH}_4)\text{I}}$) was assumed to be identical to the average isotopic composition of C_3 plants ($\delta^{13}\text{C} = -28$ ‰, $\delta^2\text{H} = -100$ ‰; Schoell, 1984).

4. Additional Data (Displayed in Figures)

Figures 1c and 2c also show the isotopic composition of n -alkanes previously identified to be abiotic in origin. These include data from (ultra)mafic hydrothermal systems (Lost City: Proskurowski *et al.* (2006), unsedimented mid-ocean ridges: McCollom and Seewald (2007), Socorro: Taran *et al.* (2010)), continental volcanic-hydrothermal systems (Milos: Botz *et al.* (1996)), ophiolites (Zambales: Abrajano *et al.* (1988), Chimaera: Etiope *et al.* (2011), inclusions in igneous rocks (Khibina: Potter *et al.* (2004), Potter and Longstaffe (2007), Lovozero: Potter *et al.* (2004)), old cratons (Kidd Creek, Driefontein, Kloof, Copper Cliff, Mponeng: all Sherwood Lollar *et al.* (2006), Sudbury, Elliott Lake, Red Lake, Juuka, Pori: all Sherwood Lollar *et al.* (1993)) and from cold (hyper)alkaline springs (Al Khoud Nizwa: Fritz *et al.* (1992), Genova: Boschetti *et al.* (2013), Othrys: Etiope *et al.* (2013a), Cabeco de Vide: Etiope *et al.* (2013b), Happon: Suda *et al.* (2014), Al Farfar: Etiope *et al.* (2015), Ronda: Etiope *et al.* (2016)). Craton gases and (hyper)alkaline spring gases with a predominant microbial contribution were excluded, as was previously done in the correlation plots of $\delta^2\text{H}\text{-CH}_4$ vs. $\delta^{13}\text{C}\text{-CH}_4$ compiled by Etiope and Sherwood Lollar (2013) and Etiope (2017).



Supplementary Tables

Table S-1 The major characteristics of the investigated volcanic-hydrothermal systems.

Country	Geothermal system	Tectonic setting	Rocks	T _{res} ^a (°C)	Source of external waters ^b	References
Alaska, USA	Trident	subduction	andesitic, dacitic	380	MW	Lopez <i>et al.</i> (2017)
	Mageik		andesitic, dacitic	260	MW	Lopez <i>et al.</i> (2017)
Argentina	Domuyo	subduction	andesitic, rhyolitic	220-240	MW	Tassi <i>et al.</i> (2016)
	Copahue		basaltic-andesitic, dacitic	250	MW	Tassi <i>et al.</i> (2017)
Azores, Portugal	Furnas	mid-ocean rifting/mantle plume	trachyte	200-275	MW	Caliro <i>et al.</i> (2015), Moore (1990)
Greece	Nisyros	subduction	andesitic, dacitic, rhyolitic	290-340	SW	Chiodini <i>et al.</i> (1993), Brombach <i>et al.</i> (2003) Fytikas <i>et al.</i> (1989)
	Santorini		andesitic, dacitic, rhyolitic	unknown	unknown	
Iceland	Reykjanes	mid-ocean rifting/mantle plume	basalts	260-345	SW	Stefánsson <i>et al.</i> (2017)
	Svartsengi		basalts	220-260	SW+MW	Stefánsson <i>et al.</i> (2017)
	Krýsuvík		basalts	220-320	MW	Stefánsson <i>et al.</i> (2017)
	Krafla		basalts, rhyolites	200-440	MW	Stefánsson <i>et al.</i> (2017)
	Námafjall		basalts, rhyolites	220-320	MW	Stefánsson <i>et al.</i> (2017)
	Hengill		basalts	200-380	MW	Stefánsson <i>et al.</i> (2017)
	Hveragerdi		basalts	170-230	MW	Stefánsson <i>et al.</i> (2017)
	Torfajökull		rhyolites	260-310	MW	Stefánsson <i>et al.</i> (2017)
	Kverkfjöll		rhyolites	260-300	MW	Stefánsson <i>et al.</i> (2017)
	Kverkfjöll		basalts, rhyolites	290-350	MW	Stefánsson <i>et al.</i> (2017)
	Askja		basalts, rhyolites	180-350	MW	Stefánsson <i>et al.</i> (2017)
Italy	Vulcano beach	subduction	leucite tephrites, trachytes, alkali-rhyolites	230	SW+MW	Chiodini <i>et al.</i> (1995), Keller (1980)
	Ischia		shoshonites, alkalitrachytes	250-300	MW	Panichi <i>et al.</i> (1992), Chiodini <i>et al.</i> (2004) Caliro <i>et al.</i> (2007, 2014)
	C. Flegrei		shoshonite, phonolites, trachytes	200-360	MW	
	Vesuvio	continental extensional	leucite-basalts, trachytes, leucitic tephrites, leucitic phonolites	360-450	MW	Chiodini <i>et al.</i> (2001)
	Pantelleria		trachytes, peralalkaline rhyolites	250	MW	Parello <i>et al.</i> (2000)



Table S-1 continued

Country	Geothermal system	Tectonic setting	Rocks	T _{res} ^a (°C)	Source of external waters ^b	References
New Zealand	Ohaaki	subduction	rhyolites, greywacke	275-310	MW	Giggenbach (1995), Christenson <i>et al.</i> (2002)
	Rotokawa		andesites, dacites, rhyolites, greywacke	290-340	MW	Giggenbach (1995), Sewell <i>et al.</i> (2015)
	Ngatamariki		basalt, andesite, rhyolite, greywacke, tonalite	260-285	MW	Giggenbach (1995), Chambefort <i>et al.</i> (2016)
Tenerife, Spain	Teide	mantle plume	basalt, trachytes, phonolites	285-316	MW	Melian <i>et al.</i> (2012)

^a reservoir temperature either measured directly or inferred from gas concentration geothermometers; ^b origin inferred from oxygen and hydrogen isotope data [see references]



Table S-2 Well data: Reservoir temperatures, sampling temperatures, carbon isotope composition of methane, ethane, propane and *n*-butane, hydrogen isotope composition of methane, steam and liquid water. Carbon and hydrogen isotope data are reported in ‰-deviation relative to VPDB and VSMOW, respectively.

Sample #	Location	Date	T _{res} ^a (°C)	T _s ^b (°C)	δ ¹³ C-CH ₄	δ ² H-CH ₄	δ ¹³ C-C ₂ H ₆	δ ¹³ C-C ₃ H ₈	δ ¹³ C- <i>n</i> -C ₄ H ₁₀	δ ¹³ C-CO ₂ (v)	δ ² H-H ₂ O(v)	δ ² H-H ₂ O(l)
<i>Iceland</i>												
Kr w32	Krafla	27/08/2015	249	178	-39.4	-314	-33.9	-28.4	-24.9	-3.8	-82	-84
Kr w16	Krafla	27/08/2015	264	203	-37.6	-239	-36.4	-32.3		-3.5	-83	-90
Kr w34	Krafla	28/08/2015	264	200	-37.5	-220	-28.4	-24.2		-4.2	-82	-86
Kr w34	Krafla	06/08/2016	264	200	-36.3	-226	-32.9	-24.7	-22.1	-4.3	-81	-83
Kr w37	Krafla	06/08/2016	295	175	-38.2	-251	-35.3	-27.3	-27.1	-4.2	-83	
Kr w31	Krafla	06/08/2016	297	148	-36.6	-224	-27.9	-18.3		-3.4	-82	
Kr w36	Krafla	06/08/2016	241	189	-34.0	-233	-32.8	-25.3		-4.8	-83	-86
Kr w27	Krafla	06/08/2016	243	183	-39.0	-293	-34.8	-24.7	-23.2	-2.9	-83	-83
Rey w15	Reykjanes	02/09/2015	281	212	-31.5	-162	-18.1	-19.0	-20.0	-2.8	-28	-12
Rey w12	Reykjanes	02/09/2015	299	220	-29.6	-150	-17.1	-17.3	-18.3	-2.8	-26	-23
Rey w12	Reykjanes	12/08/2016	299	207	-29.3	-152	-17.6	-17.0	-16.9	-3.0	-27	-20
Rey w18	Reykjanes	12/08/2016	277	217	-32.0	-172	-19.7	-22.0	-23.3	-2.6	-27	-22
Rey w11	Reykjanes	12/08/2016	305	226	-24.6	-138	-16.2	-15.9	-15.9	-3.0	-24	-20
Nam w13	Námafjall	27/08/2015	290	173	-37.2	-259	-32.1	-25.0		-3.7	-95	-93
Nam w13	Námafjall	05/08/2016	285	126	-36.1	-263	-32.2	-25.0		-3.9	-98	-90
Nam w9	Námafjall	27/08/2015	236	184	-35.4	-288	-35.1	-23.9	-22.2	-3.0	-89	-95
Nam w9	Námafjall	05/08/2016	234	175	-34.8	-283	-34.8	-22.9	-20.9	-3.2	-89	-94
Sv w9	Svartsengi	11/08/2016	240	192	-30.4	-188	-18.7	-18.9	-19.4	-2.3	-29	-20
Sv w11	Svartsengi	11/08/2016	240	204	-30.6	-183	-17.9	-17.3	-17.7	-2.8	-28	-19
<i>New Zealand</i>												
BR 67	Ohaaki	01/03/2017	304	192	-26.0	-140	-20.5	-20.2		-7.6	-45	-39
BR 56	Ohaaki	01/03/2017	268	174	-26.4	-142	-22.5	-23.7	-25.9	-6.9	-45	-39



Table S-2 continued

Sample #	Location	Date	T _{res} ^a (°C)	T _s ^b (°C)	δ ¹³ C-CH ₄	δ ² H-CH ₄	δ ¹³ C-C ₂ H ₆	δ ¹³ C-C ₃ H ₈	δ ¹³ C- <i>n</i> -C ₄ H ₁₀	δ ¹³ C-CO ₂ (v)	δ ² H-H ₂ O(v)	δ ² H-H ₂ O(l)
BR 49	Ohaaki	01/03/2017	289	177	-25.3	-142	-22.2	-21.4		-7.2	-45	-39
RK 26	Rotokawa	02/03/2017	293	248	-25.1	-144	-25.0	-28.1	-27.8	-5.5	-43	-44
RK 34	Rotokawa	02/03/2017	289	245	-25.3	-140	-15.6	-17.5	-17.1	-7.3	-41	-44
RK 14	Rotokawa	02/03/2017	316	236	-25.8	-141	-26.5	-26.9	-26.9	-6.6	-44	-42
RK 17	Rotokawa	02/03/2017	300	245	-25.4	-142	-19.8	-21.2	-22.7	-5.8	-45	-44
NM 5	Ngatamarigi	03/03/2017	287	216	-25.5	-147	-22.5	-21.5	-21.3	-6.4	-42	-40
NM 7	Ngatamarigi	03/03/2017	287	224	-25.0					-6.0	-46	-42
NM 12	Ngatamarigi	03/03/2017	284	224	-24.8	-146	-22.0	-18.3	-17.8	-5.8	-43	-43

^a T_{res} = reservoir temperature calculated assuming adiabatic boiling and using quartz geothermometry; ^b T_s = Sampling temperature;



Table S-3 Fumarole data: Vent temperatures, carbon isotope composition of methane, ethane, propane and *n*-butane, hydrogen isotope composition of methane and water vapour. Carbon and hydrogen isotope data are reported in ‰-deviation relative to VPDB and VSMOW, respectively.

Sample	Location	Date	T _v ^a (°C)	δ ¹³ C-CH ₄	δ ² H-CH ₄	δ ¹³ C-C ₂ H ₆	δ ¹³ C-C ₃ H ₈	δ ¹³ C- <i>n</i> -C ₄ H ₁₀	δ ¹³ C-CO ₂ (v)	δ ² H-H ₂ O(v)
Italy										
Vasca Ippo	Vulcano	Jun 16		-5.2	-82	-22.3	-26.1	-26.3	-2.9	-9
Vasca Ippo Centr.	Vulcano	04/10/16	102	-5.4	-84	-24.4	-24.6	-25.3	-3.2	-9
Vasca Ippo Est.	Vulcano	04/10/16	100	-5.2	-84	-20.1	-23.3		-3.6	-7
Vasca Vecchia	Vulcano	04/10/16	100	-4.8	-85	-17.0			-3.6	-11
FG	Pantelleria	02/10/13	98	-17.7	-125	-21.8			-4.1	-36
Pisciarelli	C. Flegrei	02/09/13	98	-20.5	-157	-19.2			-1.2	-17
BG	C. Flegrei	02/09/13	163	-17.2	-143	-17.8			-1.2	-21
BN	C. Flegrei	02/09/13	157	-18.5	-142	-17.8			-0.8	-26
FC2	Vesuvio	03/09/13	97	-17.7	-106	-17.3			0.4	-26
DR2	Ischia	04/09/13	100	-32.4	-213	-27.1	-27.3	-27.1	-3.8	-47
Greece										
S4	Nisyros	04/06/13	100	-23.3	-118	-18.0	-18.0	-17.9	-1.0	-4
S15	Nisyros	04/06/13	100	-22.5	-118	-18.2	-18.0		-1.0	-6
PP9S	Nisyros	05/06/13	100	-21.9	-118	-18.6	-19.6		-0.3	-7
K7	Nisyros	06/06/13	99	-22.5	-119	-18.4	-18.4		-1.3	-13
A13	Nisyros	05/06/13	99	-23.3	-131	-21.3	-19.6	-18.9	-0.4	5
Nea Kameni	Santorini	06/04/16		-31.5		-26.0	-20.8			
Tenerife										
FC	Teide	16/06/13		-8.7	-111	-18.2			-3.6	data from Melian <i>et al.</i> (2012) -47
Azores										
Furnas B	Furnas village	06/01/15	65	-64.7	-309	-30.7	-29.9			data from Caliro <i>et al.</i> (2015) -25
Furnas B	Furnas village	24/07/15	74	-63.1	-304	-31.3	-30.7		-4.1	-25
Furnas B2	Furnas village	24/07/15	74	-20.2	-127	-29.8	-29.7		-4.1	-25
Furnas B3	Furnas village	24/07/15	98	-19.4	-125	-29.0	-29.4		-4.1	-25
Furnas D	Furnas village	24/07/15	98	-19.9	-130	-29.8	-29.8		-4.2	-25
Esguicho	Furnas village	28/11/13	95	-17.9		-28.4	-28.9	-28.2	-4.3	-25
Esguicho	Furnas village	23/07/15	98	-18.5	-117	-28.4	-29.2			-25
Caldeira Seca	Furnas village	28/11/13	99	-18.7		-28.8	-27.1	-27.5	-4.2	-25
Caldeira Seca	Furnas village	06/01/15		-17.8	-119	-28.4	-27.0			-25
Caldeira Seca	Furnas village	23/07/15	97	-19.5	-126	-28.8	-27.5		-4.1	-25



Table S-3 continued

Sample	Location	Date	T _v ^a (°C)	δ ¹³ C-CH ₄	δ ² H-CH ₄	δ ¹³ C-C ₂ H ₆	δ ¹³ C-C ₃ H ₈	δ ¹³ C- <i>n</i> -C ₄ H ₁₀	δ ¹³ C-CO ₂ (v)	δ ² H-H ₂ O(v)
Dos Vimes	Furnas village	24/07/15	94	-19.3	-135	-29.4	-30.8			-25
Furnas Lake	Furnas lake	28/11/13	97	-35.9		-23.3	-26.2		-4.8	-23
Furnas Lake	Furnas lake	06/01/15	97	-34.8	-168	-22.1				-23
Furnas Lake	Furnas lake	25/07/15	98	-26.9	-135	-22.1	-23.6		-4.5	-23
Furnas Lake 4	Furnas lake	25/07/15	96	-27.4	-138	-22.1	-23.8		-4.5	-23
Furnas Lake 2	Furnas lake	28/11/13	89	-64.7		-24.8	-26.8		-6.9	-23
Furnas Lake 2	Furnas lake	06/01/15	97	-64.5	-241	-24.3				-23
Furnas Lake 2	Furnas lake	25/07/15	93	-63.3	-238	-24.0	-26.5		-4.4	-23
<i>Iceland</i>										
15-AS-01	Krýsuvík	24/08/15		-35.2	-203	-29.0	-20.6		-3.2	
15-AS-02	Krýsuvík	24/08/15		-36.1	-200	-31.6				
15-AS-03	Kerlingafjöll	25/08/15		-24.3	-196	-31.0			-3.2	
15-AS 04	Kerlingafjöll	25/08/15		-24.3	-195	-30.7			-3.3	
15-AS-05	Kerlingafjöll	26/08/15		-26.1	-200	-32.2			-3.1	
15-AS-06	Kerlingafjöll	26/08/15		-25.6	-196	-32.5			-3.0	
15-AS-11	Námafjall	28/08/15		-34.3	-297	-32.0	-25.5			
16-AS-08	Námafjall	07/08/16		-33.5	-265	-24.2	-21.8		-3.0	-109
16-AS-09	Námafjall	07/08/16		-34.3	-267	-24.9	-21.4		-3.2	-108
16-AS-10	Hengill	09/08/16		-28.6	-236	-36.9	-34.6		-3.6	-65
16-AS-11	Hveragerdi	09/08/16		-32.8	-252	-41.8	-29.9		-3.5	-67
16-AS-12	Hveragerdi	09/08/16		-25.5	-185	-37.4	-29.1	-27.2	-3.1	-64
17-TORF-1	Torfajökull	07/08/17		-32.5	-230	-35.1	-28.2	-28.2	-6.5	
17-TORF-2	Torfajökull	07/08/17		-30.6	-210	-32.9	-25.5	-30.6		
17-KVE-1	Kverkfjöll	06/09/17		-33.6	-226	-44.1	-29.9	-24.2		
17-KVE-2	Kverkfjöll	06/09/17		-33.9	-219	-43.5	-30.5	-24.8		
17-ASK-1	Askja	07/09/17		-43.3	-320	-38.7	-27.2			
17-ASK-3	Askja	07/09/17		-39.2	-293	-37.5				
<i>Alaska</i>										
MGK1	Mageik	12/07/13	92	-30.5		-27.5	-26.3	-25.8	-8.8	
TRI1	Trident	16/07/13	94	-20.2		-23.8	-22.6		-11.0	



Table S-3 continued

Sample	Location	Date	T _v ^a (°C)	δ ¹³ C-CH ₄	δ ² H-CH ₄	δ ¹³ C-C ₂ H ₆	δ ¹³ C-C ₃ H ₈	δ ¹³ C- <i>n</i> -C ₄ H ₁₀	δ ¹³ C-CO ₂ (v)	δ ² H-H ₂ O(v)
	<i>Argentina</i>									
Bramadora	Domuyo	01/03/14	107	-29.6		-19.4	-19.7			
Anfiteatro	Copahue	11/03/14	94	-36.0		-23.4	-18.3		-6.5	
Las Maquintas	Copahue	04/03/14	131	-27.9		-21.7	-18.3	-18.2	-7.6	
Las Maquinas	Copahue	04/03/14	94	-26.4		-20.9	-18.8		-7.6	
Pedra de Copahue	Copahue	06/03/14	93	-27.0		-21.2	-19.5		-7.5	
Chanco-Co	Copahue	07/03/14	95	-29.6		-19.4			-8.8	

^a T_v = Vent temperature

Supplementary Figures

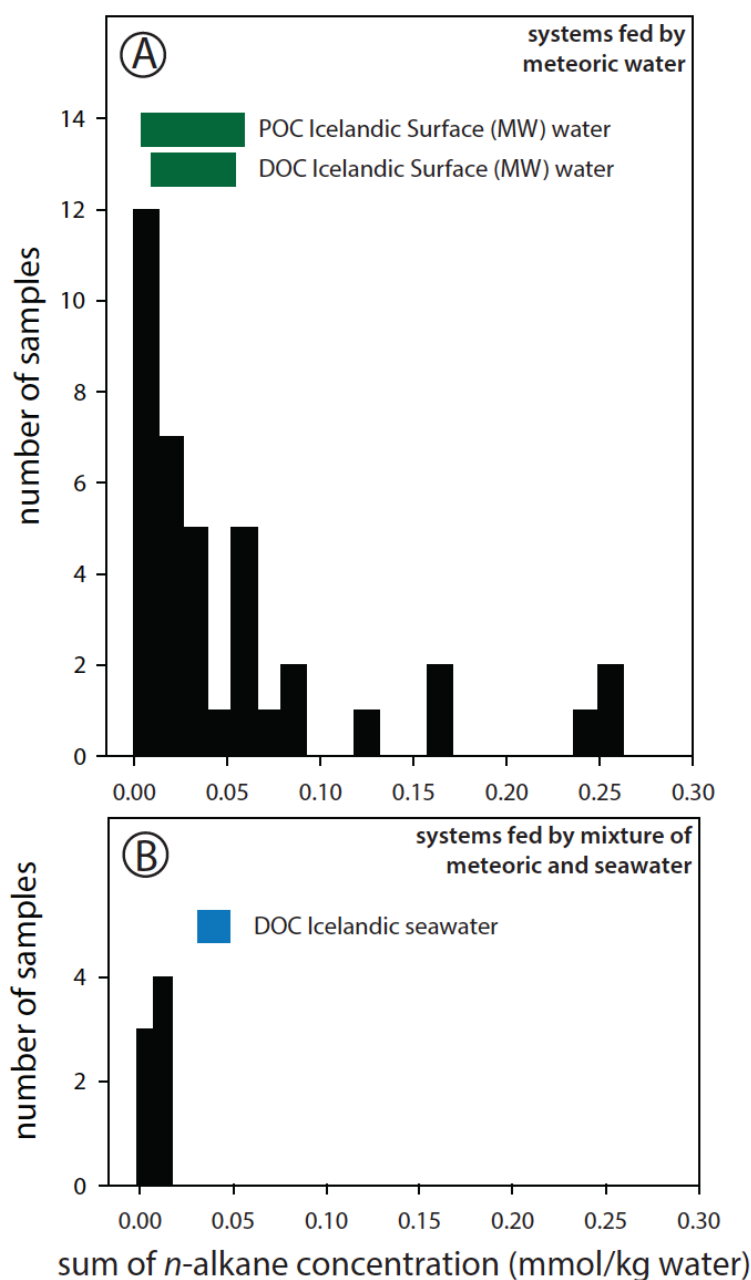


Figure S-1 The concentration of *n*-alkanes in volcanic-hydrothermal fluids in Iceland. Systems sourced by **(a)** meteoric water and **(b)** a mixture of meteoric water and seawater. Also shown are the ranges of concentrations of DOC in non-thermal meteoric surface waters in Iceland (Eiríksdóttir *et al.*, 2016; Cliffard *et al.*, 2018) and DOC and POC for seawater in Iceland (Fontela *et al.*, 2016). Total concentrations of *n*-alkanes (sum of methane, ethane, propane and *n*-butane) in the hydrothermal fluids are generally below the concentrations of organic matter in the source fluids. The volcanic-hydrothermal systems in Iceland are of recent geological age and characterised by the absence of organic sediments. For more complex systems, with multiple phase relationships (vapour, liquid, brine and halite) like sub-seafloor systems, and those associated with sedimentary deposits within the reservoir, mass balances are, however, difficult to constrain.

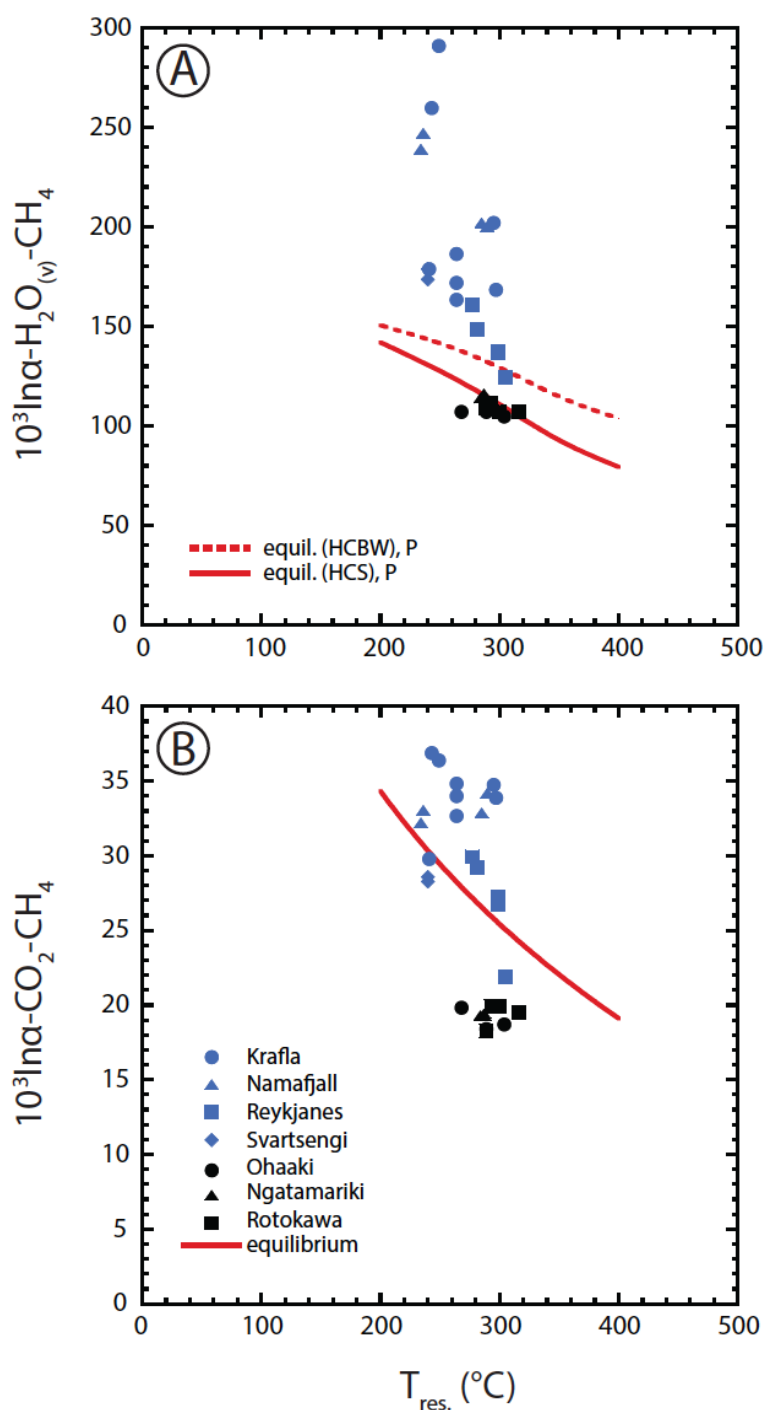


Figure S-2 Apparent isotope fractionations vs. well reservoir temperatures. All well reservoir temperatures were determined from quartz-solute thermometry (Gunnarsson *et al.*, 2000). **(a)** $1000 \ln \alpha(\text{H}_2\text{O}_{(v)}-\text{CH}_4)$ vs. reservoir T . Hydrogen isotope equilibrium is marked by red lines. HCBW combines the theoretical H_2 - $\text{H}_2\text{O}_{(v)}$ (Bardo and Wolfsberg, 1976) with the experimental CH_4 - H_2 fractionation (Horibe and Craig, 1995), whereas HCS is based on a combination of the experimental H_2 - $\text{H}_2\text{O}_{(v)}$ (Suess, 1949) with the experimental CH_4 - H_2 fractionation (Horibe and Craig, 1995). Both the theoretical and experimental H_2 - $\text{H}_2\text{O}_{(v)}$ fractionations were corrected for a density effect (Driesner, 1997) considering that gaseous water molecules above 200°C do not behave ideal, but form polymers. For further information see Supplementary Information. The size of the markers roughly corresponds to analytical precisions of isotope analyses. Data implies that hydrogen isotope equilibrium between CH_4 and water is attained at highest reservoir temperatures of $\geq 300^{\circ}\text{C}$. Isotope fractionation associated with steam separation seems to be of minor importance only since the hydrogen isotopic composition of the steam always corresponds to that of the discharged liquid water (Table S-2). **(b)** $1000 \ln \alpha(\text{CO}_2-\text{CH}_4)$ vs. reservoir temperature. Carbon isotope equilibrium (Horita, 2001) is marked by the red line. There is no indication that apparent carbon isotope fractionations vary with reservoir temperature and attain equilibrium.

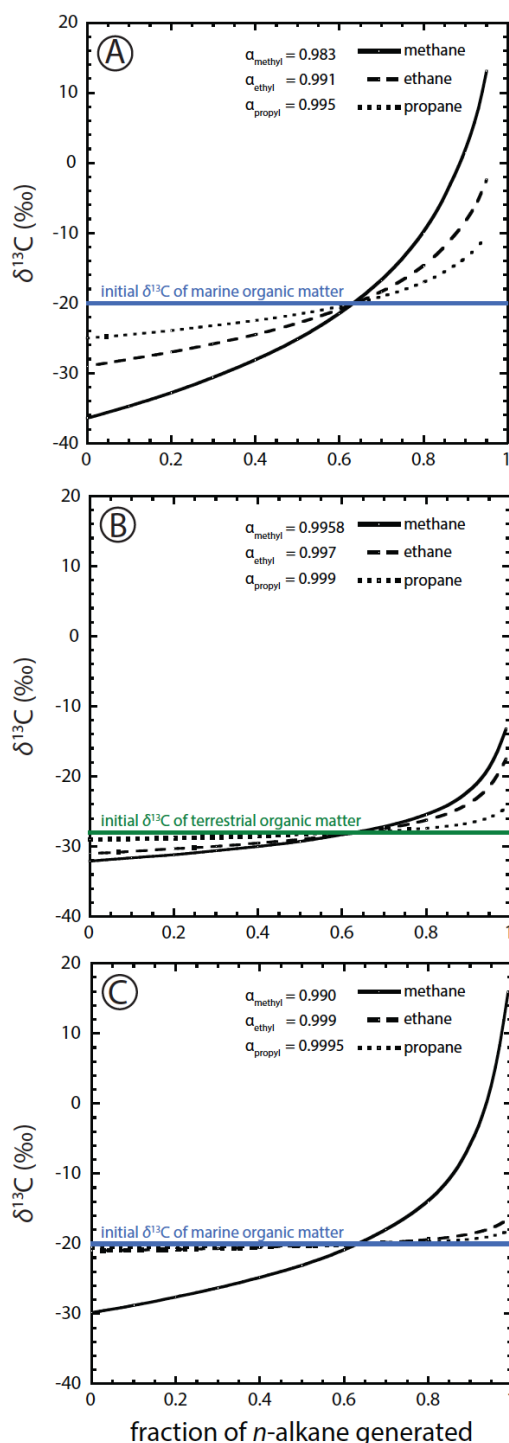


Figure S-3 $\delta^{13}\text{C}$ of instantaneous methane, ethane and propane as a function of generated fraction of n -alkane. Methane, ethane and propane derive from different precursor sites within the organic matter, and each generated n -alkane is characterised by its own specific carbon isotope fractionation factor with respect to its precursor site (for further information see Supplementary Information). During progressive cracking, instantaneous fractions of methane can become highly enriched in ^{13}C and finally even exhibit a carbon isotope reversal with respect to ethane. **(a)** $\delta^{13}\text{C}$ of the initial precursor sites corresponds with -20‰ to the average carbon isotopic composition of marine DOC. Carbon isotope fractionation factors between precursor sites in the organic matter and the respective n -alkanes correspond to those determined from pyrolysis of marine kukersite (Berner *et al.*, 1995). According to these experiments methane from marine organic matter may have the potential to become highly enriched in ^{13}C during late stage cracking (fraction of generated methane $\rightarrow 1$). **(b)** $\delta^{13}\text{C}$ of the initial precursor sites corresponds with -28‰ to the average carbon isotopic composition of terrestrial C_3 plants. Carbon isotope fractionation factors between precursor sites in the organic matter and the respective n -alkanes correspond to those determined from pyrolysis of terrestrial xylite (Berner *et al.*, 1995). **(c)** $\delta^{13}\text{C}$ of the initial precursor sites corresponds with -20‰ to the average carbon isotopic composition of marine DOC. Carbon isotope fractionation factors between precursor sites in marine organic matter and the respective n -alkanes chosen to match $\delta^{13}\text{C}$ of Reykjanes n -alkanes ($\delta^{13}\text{C}\text{-CH}_4$ around -30‰ ; $\delta^{13}\text{C}\text{-C}_{2+}$ invariant and close to -20‰ , Table S-2) at the very early stage of degassing (fraction of generated n -alkane $\rightarrow 0$).



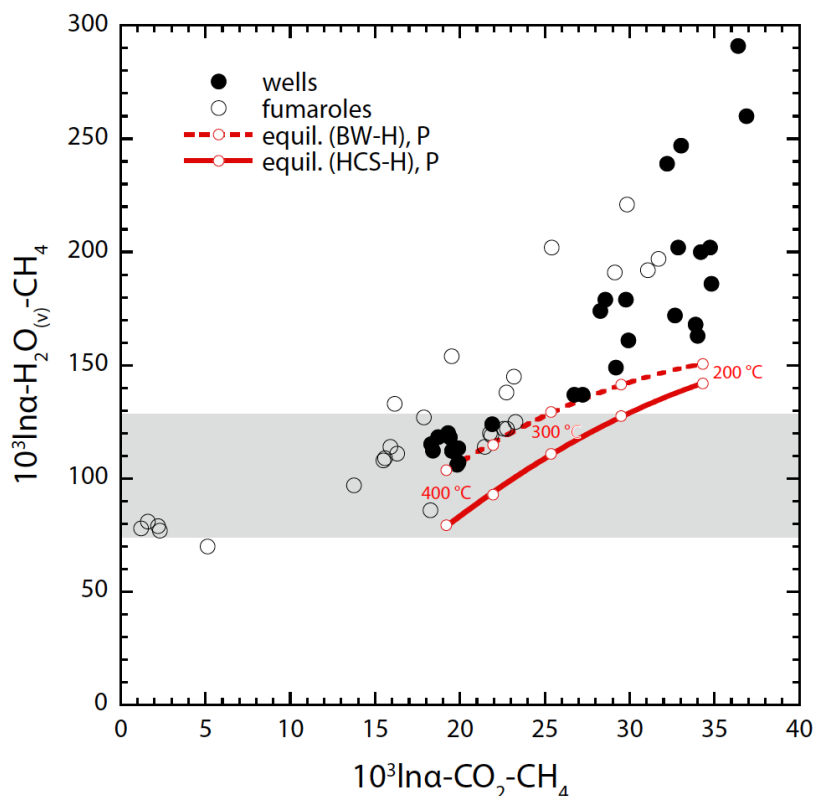


Figure S-4 Plot of apparent carbon ($\text{CO}_2\text{-CH}_4$) against apparent hydrogen ($\text{H}_2\text{O}_{(v)}\text{-CH}_4$) isotope fractionation. For calculation of displayed equilibrium isotope fractionations see Fig. S-2 and Supplementary Information. Isotopic data for calculation of apparent isotopic fractionations are taken from Tables S-2 and S-3. The grey shaded field indicates hydrothermal temperatures ≥ 300 °C, i.e. a range within which hydrogen isotope equilibrium between $\text{H}_2\text{O}_{(v)}$ and CH_4 might be attained, as implied by Fig. S-2a. Within this range, the apparent hydrogen isotope fractionation between $\text{H}_2\text{O}_{(v)}$ and CH_4 corresponds to reasonable hydrothermal temperatures (up to 450 °C, Table S-1). Within the same range the apparent $\text{CH}_4\text{-CO}_2$ isotope fractionation is largely variable and extends to very small values corresponding to temperatures exceeding 1000 °C. This provides additional evidence that the apparent carbon isotope fractionation between CO_2 and CH_4 only fortuitously corresponds to equilibrium in some systems. During the stage where either the hydrogen isotopic composition of methane or that of the decomposing organic matter at depth becomes buffered by the isotopic composition of water, methane is further distilled out of the system, leaving the methane precursor sites in the organic matter and, hence, the instantaneous fractions of generated methane progressively enriched in ^{13}C .

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