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

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Abstract

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

Introduction

The ability to distinguish between biotic and abiogenic 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 abiogenic 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., Ettorre and Sherwood Lollar, 2013; Etiope and Schoell, 2014). Abiogenic 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., Ettorre and Sherwood Lollar, 2013; Etiope and Schoell, 2014).

Most prominently, the following criteria have been used to identify abiogenic hydrocarbon occurrences: i) methane with δ13C ≥ –20 ‰ (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 abiogenic 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
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 C3 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 (C2, hydrocarbons), with variations in δ13C-C2 ≤ 1.0‰ (Fig. 1a). At Reykjanes, δ13C-C2, of −16‰ (well 11) and −17 to −18‰ (well 12) overlap with the carbon isotopic composition of particulate organic carbon (−17.5‰ ≥ δ13C-POC ≥ −22.2‰) and modern sedimentary organic matter (−16.5‰ ≥ δ13C-SOM ≥ −19.4‰) that are characteristic of the water masses surrounding the Reykjanes peninsula (Sara et al., 2007). For Esguicho (Furnas village) δ13C-C2, 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 δ13C-C2, but absolute values changing with the source of water - are observed at Nisyros (seawater-fed hydrothermal system, δ13C-C2, around −18‰), Ischia and Rotokawa well 14 (both meteoric water-fed systems, δ13C-C2, 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 C2 hydrocarbons and the source organic matter becomes insignificantly small and, hence, the δ13C-C2 becomes indicative of the bulk organic matter decomposing at depth.

Thermogenic C2 hydrocarbon production is not restricted to systems with invariant δ13C-C2, but is most likely important in all systems. Although the majority of sampled discharges exhibit significant differences among δ13C-C2 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‰ ≥ δ13C-DOM ≥ −23‰; Druffel et al., 1992), modern marine particulate organic carbon (−17‰ ≥ δ13C-POC ≥ −25‰; Druffel et al., 1992; Sara et al., 2007) and modern terrestrial C3 plants (−20‰ ≥ δ13C ≥ −37‰, with most data clustering between −23‰ ≥ δ13C ≥ −31.5‰ and averaging at δ13C = −28.5‰; Kohn, 2010) (Fig. 1b). Moreover, relative variations in δ13C 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
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 δ²⁰⁹⁰C-CH₄ and δ²⁰²⁰H-CH₄ 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 δ²⁰⁹⁰C-CH₄ samples from meteoric water-fed hydrothermal systems (green data points), but – on average – occurs shifted relative to the latter to higher δ²⁰⁹⁰C and δ²⁰²⁰H. This implies that methane precursor sites in decomposing terrestrial organic matter either occur depleted in δ²⁰⁹⁰C and δ²⁰²⁰H with respect to the average C₃ plant isotopic composition or that the corresponding carbon and hydrogen isotope fractionations (α₉C, α₉H) are larger than those obtained from xylite (Berner et al., 1995), with α₉C, α₉H 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).

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 δ¹³C and δ²⁰²⁰H; Whiticar et al., 1999) are excluded, methane still exhibits the largest variations in δ¹³C of all analysed n-alkanes (Fig. 1b). Second, in δ¹³C vs. δ²⁰H 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 δ¹³C 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 δ¹³C-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 δ¹³C 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 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 δ¹³C-C-CH₄, data (Table S-2). Although the Rotokawa hydrothermal reservoir is exclusively sourced by meteoric waters (Table S-1), its δ¹³C-n-C₄ 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).

Figure 2: Plot of δ²⁰H-CH₄ vs. δ²⁰⁹⁰C-CH₄. Samples with an obvious microbial origin (δ²⁰⁹⁰C-CH₄ < -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


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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-3). 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 13C) through the reservoir should, therefore, be higher in well systems. This is consistent with the observation that well discharges display on average lower δ13C-CH4 values than fumaroles (Fig. 2b).

Two reasons may account for δD departing from the predicted cracking and degassing trends at high organic matter maturities characterised by δ13C-CH4 ≈ −20 ‰ (Fig. 2a). First, hydrogen isotope exchange between CH4 and water may occur at the elevated temperatures characteristic of hydrothermal systems, driving CH4 towards isotopic equilibrium with water at T ≥ 300 °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, δ13C-CH4 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 δ13C-CH4 is controlled by the relative fluxes of organic carbon into and methane carbon out of the system, carbon isotope equilibrium between CH4 and CO2 might not be attained, such that the apparent fractionation would only fortuitously correspond to equilibrium in some cases (Figs. S-2b, S-4).

Conclusions

δD and δ13C of CH4 as well as δ13C of C2n as n-alkanes from volcanic-hydrothermal emissions follow isotopic trends that are consistent with the principles of organic matter degredation 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 13C 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

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References


