



Isotopic patterns of hydrothermal hydrocarbons emitted from Mediterranean volcanoes



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ABSTRACT

We have analyzed the carbon isotopic composition of CO₂, methane, ethane, propane and n-butane, the hydrogen isotopic composition of methane as well as total concentrations of gas constituents contained in the Mediterranean volcanic–hydrothermal discharges of Nisyros (Greece), Vesuvio, La Solfatara, Ischia and Pantelleria (all Italy) to determine the origin of the hydrocarbons. Isotopic criteria conventionally used for hydrocarbon classification suggest thermogenic origins, except for Pantelleria, for which an abiogenic origin is indicated. These findings would imply that thermogenic sources can provide methane/(ethane + propane) concentration ratios as high as those usually observed for microbial hydrocarbons. However, additional consideration of gas concentration data challenges the suitability of conventional criteria for the classification of hydrocarbons emanating from hydrothermal environments. Methane seems to be in close equilibrium with co-occurring CO₂, whereas its higher chain homologues are not. Therefore, it cannot be excluded that methane on the one hand and ethane, propane and n-butane on the other hand have distinct origins. The carbon isotopic composition of methane might be controlled by the carbon isotopic composition of co-occurring inorganic CO₂ and by hydrothermal temperatures whereas the carbon isotopic composition of the higher n-alkanes could correspond to the maturity of organic matter and/or to the residence time of the gasses in the source system.

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1. Introduction

Hydrothermal systems around the world commonly discharge trace amounts of hydrocarbons such as n-alkanes, n-alkenes and aromatics along with CO₂ (Capaccioni et al., 1993; Darling, 1998; Taran and Giggenschbach, 2003; Tassi et al., 2005, 2012). Potential sources of CO₂ are the mantle, crustal carbonates and organic compounds. Relative contributions of these sources to overall CO₂ production can be determined using a correlation between CO₂/³He ratios and the carbon isotopic composition of the CO₂ (Sano and Marty, 1995). There is, however, no such clear indicator for identifying the sources contributing to overall hydrocarbon production. Methane is primarily produced biogenically by 1) processes related to metabolic and biosynthetic activity of microbes, such as acetate fermentation and CO₂ reduction, and 2) thermogenic decomposition of organic matter buried in sediments (Schoell, 1980, 1988; Rice and Claypool, 1981; Whiticar et al., 1986; Oremland et al., 1987; Whiticar, 1999). Microbial methane production is possible up to temperatures of at least 122 °C (Takai et al., 2008), whereas thermogenic gas generation starts with cracking of oil at > 150 °C (Quigley and MacKenzie, 1988). Under laboratory conditions, both CH₄ and its

higher chain homologues can be produced abiogenically (i.e., in the absence of organic matter) through mechanisms that may include Fischer–Tropsch-type (FTT) reactions (Fischer and Tropsch, 1926) at temperatures above 200 °C, high pressures and using metal and mineral catalysts (Foustoukos and Seyfried, 2004; Fu et al., 2007; McCollom and Seewald, 2006, 2007; Taran et al., 2007, 2010a; McCollom et al., 2010). Production of CH₄ by olivine hydration at low temperature (<70 °C) and from methanation of H₂ and CO₂ mixtures at 50 °C has also been documented (Neubeck et al., 2011; Thampi et al., 1987; Jacquemin et al., 2010).

Two types of diagrams are very often used to discriminate between methane of thermogenic and microbial origins. Bernard et al. (1978) introduced a correlation between CH₄/(C₂H₆ + C₃H₈) ratios and corresponding δ¹³C-CH₄ values. In most cases, microbial CH₄ occurs significantly more depleted in ¹³C and exhibits significantly higher CH₄/(C₂H₆ + C₃H₈) ratios than thermogenic methane (e.g., Whiticar, 1999; but see also Valentine et al., 2004, and Hinrichs et al., 2006, for exceptions). The relatively low ¹³C content of microbial methane also enables discrimination between microbial and thermogenic production in a plot of δD against δ¹³C (Schoell, 1980). Methane emanating from (ultra)mafic hydrothermal systems such as Lost City and the East Pacific rise is even more enriched in ¹³C than methane from common thermogenic sources (see McCollom and Seewald, 2007, for an overview).

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These (ultra)mafic systems provide all the prerequisites that might be necessary for abiogenesis, such as CO₂, hydrogen, heat and metal catalysts. As a consequence, the carbon isotopic composition might be a criterion for identifying abiogenic methane, too. However, unless independent evidence for abiogenesis is provided, it cannot be excluded that “abiogenic” signatures were simply received from uncommon primary or secondary processes occurring within the thermogenic and/or microbial domains. For example, it should be noted that kinetically controlled oxidation (abiogenic and biogenic) strongly discriminates against the heavy isotopes leaving the residual methane enriched in ¹³C and D (Coleman et al., 1981; Kiyosu and Imaizumi, 1996; Kinnaman et al., 2007). Welhan (1988) and Etiope et al. (2011a) have pointed to the importance of secondary methane oxidation in natural environments.

Most prominently, carbon isotope patterns of n-alkanes have been used to identify potential occurrences of abiogenic hydrocarbons. A major prerequisite for its applicability is the occurrence of kinetically controlled mass exchange between methane and its higher chain homologues. Generally, ¹³C–¹²C bonds are more stable than ¹²C–¹²C bonds so that during thermal degradation of organic matter ¹²C–¹²C bonds are preferentially broken compared to ¹³C–¹²C bonds. Hence, the ¹³C content of hydrocarbons deriving from a common thermogenic source can be expected to increase with increasing carbon number n. Indeed, such carbon isotope patterns are very often revealed by hydrocarbons discharging from thermogenic sources (e.g., Chung et al., 1988; Galimov, 1988, 2006). In contrast, gasses emanating from some (ultra)mafic systems and gasses included in plutonic rocks often contain CH₄ that is enriched in ¹³C relative to its higher chain homologues (Sherwood Lollar et al., 2002; Potter et al., 2004; Proskurowski et al., 2008; Sherwood Lollar et al., 2008). Such reverse patterns were also experimentally produced via incomplete Fischer–Tropsch reaction (Lancet and Anders, 1970) and via formation of hydrocarbons from methane in a spark discharge (Des Marais et al., 1981) and might, therefore be indicative for hydrocarbon generation by abiogenic polymerization reactions. However, isotopic reversal between ethane and methane has also been observed to occur in shale gasses, i.e. gasses that were thought to originate from the thermal decomposition of organic matter (Burruss and Laughrey, 2010; Zumberge et al., 2012). The reason for the observed reversal remains unclear, but could be due to mixing of thermogenic gasses deriving from two distinct sources (Xia et al., 2013), sometimes possibly superimposed by redox reactions governing preferential removal of ethane and propane over methane (Burruss and Laughrey, 2010). In addition, hydrothermal experiments imply that reversed carbon isotope patterns between ethane and methane rather seem to be the exception than the rule for abiogenically generated hydrocarbons (McCullom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007, 2010a; McCullom et al., 2010). These findings have challenged the use of C-isotope patterns of n-alkanes as an indicator of hydrocarbon origin.

Fiebig et al. (2007) addressed the genetic relationship between CH₄ and co-discharged CO₂ to determine the origin of methane in volcanic–hydrothermal discharges. They argued that the confirmation of apparent carbon isotopic temperatures by independent gas concentration geothermometers strongly implies that CH₄ and CO₂ underneath Nisyros, Vesuvio and Ischia attained isotopic equilibrium at temperatures ranging from 250 to 470 °C. The co-emitted CO₂ at these locations represents mixtures of inorganic CO₂ aliquots deriving from the mantle and from marine limestones (Fiebig et al., 2007). Equilibrium between CH₄ and CO₂ was either attained from the oxidation of small excess amounts of methane of an unspecified origin or from the site of CO₂ reduction. In this respect, methane at Nisyros, Vesuvio and Ischia may have an abiogenic origin (Fiebig et al., 2007). However, at least at Nisyros ethane and propane are in strong chemical disequilibrium with co-discharged methane and CO₂ (Fiebig et al., 2009). It, therefore, seems that methane on the one hand and the C₂₊ n-alkanes on the other hand originate from different sources. A relatively small proportion

(<2%) might derive from the thermal decomposition of organic matter, whereas the overwhelming amount (>98%) might be represented by (almost) pure methane having attained equilibrium with inorganic CO₂ (Fiebig et al., 2009). If so, carbon isotope partitioning patterns would not be indicative for the origin of the n-alkanes in these systems, since the carbon isotopic composition of methane is controlled by thermodynamics, whereas that of the C₂₊ n-alkanes is governed by the kinetics describing cracking of organic polymers to monomers.

Volcanic–hydrothermal gasses usually contain only (sub) ppb concentrations of C₂₊ n-alkanes. Such low concentrations cannot be analyzed for their isotopic composition unless enrichment occurs in the field during sampling and/or in the laboratory. As a consequence, carbon isotope data on n-alkanes other than methane are extremely rare for these environments (e.g., Des Marais et al., 1981; Taran et al., 2010b). We have set up an enrichment technique in our laboratory that allows carbon isotope analysis of nmol amounts of hydrocarbons contained in the headspace of soda samples collected in the field (Giggenbach, 1975). Using this setup we have analyzed the carbon isotopic composition of methane, ethane, and, whenever possible, propane and n-butane contained in hydrothermal gasses collected at Nisyros (Greece), Vesuvio, La Solfatara, Ischia and Pantelleria (all Italy). We discuss the origin of the hydrocarbons in these systems, as indicated by “classical” isotopic criteria and by a synopsis of isotopic and gas concentration data. It appears that there are no unequivocal criteria for abiogenic hydrocarbon production available yet. Methane in some of the investigated systems might be abiogenic, but direct evidence is still pending.

2. Geological settings and sampling of fumarolic gasses

Nisyros, Vesuvio, La Solfatara and Ischia are all related to subductional volcanism, whereas Pantelleria is situated along an extensional system (e.g., Fytikas et al., 1976; Peccerillo, 2003, 2005). Volcanic rocks at these localities are well-evolved and widely differ in their chemical composition, covering the entire calc-alkaline and (per)alkaline series. Bi-phase hydrothermal systems occur at depths of 1–5 km at temperatures ranging from 250 °C to 550 °C. Evidence for the occurrence of hydrothermal reservoirs and their corresponding temperatures is provided by the absence of highly soluble, acid magmatic components such as SO₂, HCl and HF in the emitted gasses and by gas geothermometry (e.g., Chiodini et al., 2001; Fiebig et al., 2004; Chiodini et al., 2004; Caliro et al., 2007; Fiebig et al., 2013).

Information about the position of fumarolic vents in each of these locations are provided by Brombach et al. (2003) for Nisyros, Chiodini et al. (2001) for Vesuvio, Caliro et al. (2007) for La Solfatara, Chiodini et al. (2004) for Ischia and D’Alessandro et al. (2009) for Pantelleria. Fumarolic vent temperatures always corresponded to the boiling temperature of liquid water, with the exception of La Solfatara fumaroles BG and BN, where emission temperatures were significantly higher. In the field, volcanic gasses were collected in 125 ml glass exetainers filled with ~50 ml of 4 M NaOH soda solution (Giggenbach, 1975). Each fumarole was also sampled for dry gasses following the protocol outlined by Cioni and Corazza (1981). For the purpose of carbon isotope analysis of the C₂₊ n-alkanes, sampling campaigns were performed at Nisyros in June 2013, at Vesuvio, Ischia and La Solfatara in September 2013 and at Pantelleria in October 2013. In addition, Nisyros and Pantelleria fumaroles were sampled in October 2007 and in November 2008, respectively, for carbon and hydrogen isotope analysis of CH₄.

3. Analytical setup

In the case of the Mediterranean volcanic–hydrothermal emissions sampled in this study, absolute concentrations of methane are usually in the lower μmol range, whereas concentrations of the C₂₊ n-alkanes are even lower by a factor of 100 to 1000. If the gasses are collected with the soda bottle technique (Giggenbach, 1975) water and acid

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