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Hydrocarbons and oxidized organic compounds in hydrothermal fluids from Rainbow and Lost City ultramafic-hosted vents

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ABSTRACT

The first building blocks of life could be produced in ultramafic-hosted hydrothermal systems considering the large amounts of hydrogen and methane generated by serpentinisation and Fischer–Tropsch-Type synthesis, respectively, in those systems. The purpose of this study was to detect and characterise organic molecules in hydrothermal fluids from ultramafic-hosted hydrothermal systems in the Mid-Atlantic Ridge (MAR) region. During the EXOMAR cruise 2005, fluids from the Rainbow (36°14′N) and the Lost City (30°N) hydrothermal fields were collected and treated by Stir Bar Sorptive Extraction (SBSE) and Solid Phase Extraction (SPE). The extracts were analysed by Thermal Desorption–Gas Chromatography–Mass Spectrometry (TD–GC–MS) and GC–MS, respectively. Compared to nearby deep seawater, hydrothermal fluids were clearly enriched in organic compounds, with a more diverse spectrum of molecules. We observed a very similar range of organic compounds in fluids from both sites, with a dominance of aliphatic hydrocarbons (C9–C14), aromatic compounds (C6–C16) and carboxylic acids (C8–C18). The occurrence of these compounds is supported by other field studies on serpentinites and sulfide deposits. Literature on thermodynamic data and experimental work has suggested the possible abiogenic origin of hydrocarbons and organic acids. In addition, it has been shown elsewhere that catalytic reactions producing hydrocarbons likely occur at both Lost City and Rainbow hydrothermal fields as suggested by the evolution of $\delta^{13}C$ with increasing C number for methane, ethane, propane and butane. In order to investigate the origin of the organic molecules in the fluids, compound-specific carbon isotope ratio measurements were performed on n-alkanes and carboxylic acids, for which the $\delta^{13}C$ values were in the range of −46 to −20‰ (vs. V-PDB). These preliminary data did not allow conclusive support or rejection of an abiogenic origin of the compounds. Indeed, predicting $\delta^{13}C$ signatures in hydrothermal systems is likely to be complicated, due to differences in source $\delta^{13}C$ signatures (i.e., of the C building blocks), and a variety of, mostly unknown, fractionation steps which may occur along the synthesis pathways. In addition, even though a fraction of the compounds detected in the fluids is likely abiotically produced, a dominance of biogenic sources and/or processes might hide their characteristic signature.

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1. Introduction

The first hydrothermal systems in the Atlantic Ocean were discovered in the late 1970s. Since then, numerous hydrothermal fields, mainly located at the ridge axis, were discovered, e.g. the Trans-Atlantic Geotraverse (TAG), Lucky Strike, Menez Gwen, Broken Spur, Turtle Pits and MARK hydrothermal systems on the Mid-Atlantic Ridge (MAR). Hosted on mafic rocks, they are related to basaltic volcanism. In 1995 (MICROSMOKE cruise), on-axis ultramafic-hosted vents were first sampled along the slow-spreading MAR: the Logachev (Sudarikov and Roumiantsev, 2000) hydrothermal field was the first one discovered of a series of three known today (Logachev (Sudarikov and Roumiantsev, 2000), Rainbow (Charlou et al., 2002) and Ashadze (Serpentine-Cruise-Ifremer, 2007)). Their characteristic feature is their location on mantle outcrops consisting of peridotites, primarily composed of olivine and pyroxene. This specific location enables hydrothermal circulation to reach, and thus to alter, the mantle rocks. In particular, the reaction of interest in our case is the serpentinisation

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of peridotites. The process can be described by several reactions, one of them Eq. (1) was proposed by Bach et al. (2006).

$$2\underset{\text{olivine}}{[Mg_{1.8}Fe_{0.2}SiO_4]} + 3\,H_2O = \underset{\text{serpentine}}{[Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4]} + \underset{\text{Ferrobrucite (intermediate)}}{[Mg_{0.75}Fe_{0.25}(OH)_2]} \quad (1)$$

$$12\underset{\text{ferrobrucite}}{[Mg_{0.75}Fe_{0.25}(OH)_2]} = \underset{\text{magnetite}}{Fe_3O_4} + 9\,\underset{\text{brucite}}{Mg(OH)_2} + H_2 + 2H_2O$$

Hydrogen produced during the oxidation of olivine and reduction of water may subsequently react under hydrothermal conditions with dissolved CO_2 to produce CH_4:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (2)$$

Ultramafic-hosted hydrothermal activity (of which Rainbow is representative) is generally associated with high concentrations of reduced gaseous species (H_2 and CH_4) in the fluids (Charlou et al., 1998), as well as high temperature (250–350 °C) and low pH (3–4). Finally other hydrothermal systems were discovered off-axis along the slow-spreading MAR: The Nibelungen hydrothermal field (8°S) was sampled in 2006 (Keir et al., 2008; Melchert et al., 2008); the Lost City hydrothermal field was discovered in 2000 (Kelley et al., 2001) and is located (15 km west of the ridge axis) on the southern ridge of a dome-like massif predominantly composed of ultramafic rocks with minor gabbroic bodies. Among ultramafic-hosted vents, Lost City is one of a kind expelling low-temperature (<100 °C) alkaline (pH=10–11) fluids.

The abiogenic origin of hydrocarbons has been discussed since 1940 (Glasby, 2006) and the possibility of abiotic synthesis of organic compounds in mafic environments was already suggested in the late 1970s by Ingmanson and Dowler (1977). More recently, Charlou and Donval (1993) and Charlou et al. (1998) evidenced the cause and effect relationship between CH_4 anomalies in the water column and the presence of ultramafic rocks. In the meantime many researchers supported the abiotic synthesis hypothesis in mafic-hosted hydrothermal environment: Corliss et al. (1981), Holm (1992), Holm and Hennet (1992), Shock (1992), Simoneit et al. (1992) and Simoneit (1995). However, ultramafic-hosted systems are more favourable environments for such organic synthesis due to the strong reducing power (high H_2 concentration) of the fluids (Berndt et al., 1996; Shock and Schulte, 1998; Holm and Charlou, 2001; Kelley et al., 2002). Besides, alkaline systems such as the Lost City hydrothermal field have been predicted on the basis of a hydrothermal origin of life hypothesis (e.g. Macleod et al., 1994). Moreover, it is widely suggested that hydrocarbons could be generated by reduction of CO_2 via an aqueous Fischer–Tropsch Type (FTT) reaction. The original process involved CO as a carbon source according to the general Eq. (3).

$$(2n+1)H_2(g) + nCO(g) \rightarrow C_nH_{2n+2} + nH_2O \quad (3)$$

However the reaction will occur using other sources of carbon than CO as a reagent; typically CO_2 is available in hydrothermal systems and the mass balanced Eq. (3) becomes:

$$(3n+1)H_2 + nCO_2aq \rightarrow C_nH_{2n+2} + 2nH_2O \quad (4)$$

Numerous laboratory experiments (McCollom et al., 1999; McCollom and Simoneit, 1999; McCollom, 2000; Rushdi and Simoneit, 2001, 2004, 2005, 2006; Seewald et al., 2006) have indeed demonstrated that hydrocarbons as well as other organic compounds can be abiotically produced under hydrothermal conditions, and that the presence of a mineral catalyst is important (Chen and Bahnemann, 2000; Cody et al., 2000, 2001, 2004; Foustoukos and Seyfried, 2004; Chen and Chen, 2005). In addition, the possibility of abiotic synthesis has been supported by thermodynamic calculations (Shock, 1990, 1994; Schulte and Shock, 1995; Shock et al., 1995; McCollom and Shock, 1998; McCollom and Seewald, 2001) involving pressure, temperature and hydrogen fugacity (fH_2). These thermodynamic studies showed that kinetic barriers may prevent the inherently sluggish stable equilibria CO_2/CH_4 and N_2/NH_3 to establish in hydrothermal solutions. Moreover, sufficient redox conditions, set by fH_2, controlled in turn by the lithological assemblage (combination of different types of rocks), would stabilise metastable intermediates, i.e. organic compounds in hydrothermal solutions (Shock, 1990) (Fig. 1). Another reason for organic compounds to subsist in hydrothermal environments is that the time to reach a CO_2/CH_4 chemical equilibrium at 400 °C is expected to be ~100 years and 100,000 years at 300 °C (Giggenbach, 1982), which is much longer than the time for the fluids to move up from the high temperature deep zone to the chimney (Shock, 1990). Finally, field data show that hydrocarbons persist at temperature higher than 300 °C and fossil evidence linking organic compounds to hydrothermal circulation appears all over the planet in various environments (Shock, 1990 and references therein).

Abiotic synthesis of organic compounds may have provided material for life to start (Ferris, 1992; Simoneit, 1995) and the wide range of temperature, pressure and fluid compositions at the vent sites could be favourable for the emergence of early life forms. However, it has to be noted that even though abiotic compounds would have been generated in conditions existing in a pure hydrothermal fluid related to serpentinisation, the majority of macromolecules typical of the cell organisation are degraded under such conditions. As a consequence the reactor where abiotic molecules would have formed is likely to be different from the one where life has developed. On the other hand, experimental work under hydrothermal conditions has demonstrated the formation of several organic compounds with affinities to some of those found in living cells: methanol (Voglesonger et al., 2001), formic acid (Seewald et al., 2006), carboxylic acids (McCollom et al., 1999; Cody et al., 2000; Rushdi and Simoneit, 2001), amino acids (Ferris, 1992; Keefe et al., 1995; Huber and Wächtershäuser, 2003), purines and pyrimidines (Ferris, 1992; Saladino et al., 2001). Ribose would also be stabilised by boron at high pH (Prieur, 2001a,b; Ricardo et al., 2004). This discussion goes beyond the topic of this paper, and we refer to a number of reviews covering this topic (Ferris, 1992; Simoneit, 2004; Holm and Andersson, 2005) and the various hypotheses that have been developed on the possible evolution of life from those abiotic molecules (Nelson et al., 2000; Orgel, 2003; Ferris et al., 2004; Russell and Hall, 2006; Martin and Russell, 2007; Russell, 2007).

To the best of our knowledge, very little data have been published on the actual organic composition of pure hydrothermal fluids (Brault et al., 1988; Holm and Charlou, 2001). This lack of data is partly related to the difficulty of obtaining samples, particularly ones that are non-contaminated. In addition, preconcentration of organic compounds is needed to reach detection limits, which means that large sample

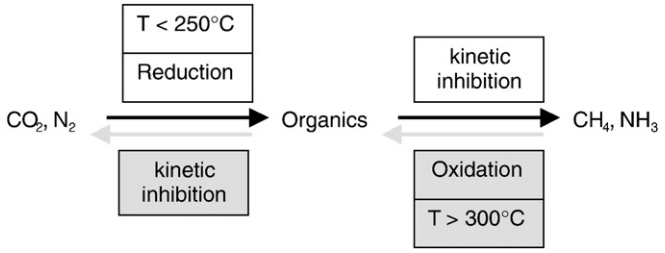

Fig. 1. Cartoon illustrating the metastable equilibrium theory among organic molecules, CO_2, N_2, CH_4 and NH_3.

volumes are required and the actual collected volumes are often too small. Moreover, the development and optimisation of sampling and analytical techniques are tedious and time-consuming. However the possibility that organic compounds occur and persist in hydrothermal fluids has been widely studied by both experiments (McCollom, 2000; Rushdi and Simoneit, 2001; Seewald et al., 2006) and modelling (Shock, 1990, 1992; Helgeson et al., in press). In addition, for the last four to five years, preliminary field data results suggested the presence of organic molecules in hydrothermal fluids (Charlou et al., 2004; Charlou et al., 2005; Konn et al., 2006). The aim of the present study is to provide a detailed overview of the organic compounds present in fluids from the Rainbow and Lost City hydrothermal fields, to highlight some biologically relevant compounds, and to discuss their possible abiotic origin.

2. Geological setting

The Rainbow hydrothermal field is located on the Mid-Atlantic Ridge (MAR), south of the Azores, at 36°14′N, 33°54′W and at a 2300 m depth (Charlou et al., 2002). It is located, geographically, on the west-facing flank of the Rainbow ridge at the north eastern corner of the south Azores Mid-Atlantic Ridge (AMAR) segment; geologically, right at the intersection of the non-transform fault system and the ridge faults. The field size is about 250 m (east–west) by 60 m (north–south) and consists of at least 10 groups of highly active black smokers, which are distributed over the entire field (Fig. 2). It is based on peridotite-rich mantle outcrops that are associated with large amounts of CH_4 (Charlou et al., 1998). These peridotites undergo serpentinisation, leading to a huge production of H_2 (Charlou et al., 2002). The temperature of the Rainbow fluids is around 360 °C (Fouquet et al., 1997) and the pH is low (pH=3–4). Furthermore, they have high chlorinity (780 mmol kg^{-1}), high metal concentrations (e.g. [Fe]=24 mmol kg^{-1}), high alkaline cation levels (Douville et al., 2002) and the concentration of dissolved SiO_2 is low. Finally high levels of dissolved hydrogen (16 mmol kg^{-1}), methane (2.5 mmol kg^{-1}) (Charlou et al., 1998, 2002), and hydrocarbons (Holm and Charlou, 2001) have been reported.

Specific features about the Lost City hydrothermal system are its off-axis position, the low-temperature and high pH fluids, and the carbonate-brucite hydrothermal chimneys. The hydrothermal activity is concentrated at the southern edge of the Atlantis Massif located 15 km west of the MAR axis at 30°07N, 42°07W (Fig. 3). The massif rises at 700 m below the sea surface and is terminated in the south by a nodal basin that is up to 6000 m deep. The latter is formed by the intersection of the Atlantis Fracture Zone and the MAR (Kelley et al., 2005). The field, which extends over 400 m in length, is composed of active, inactive, and fissure-filling carbonate formations. Früh-Green et al. (2003) have shown that hydrothermal activity has spanned over at least 30,000 years in this zone. Expelled fluids have low temperature (40–90 °C) and have a greatly different chemical composition compared to the Rainbow fluids, with high pH (10–11), and low metal and SiO_2 concentrations. CH_4 (1–2 mmol kg^{-1}) and H_2 (up to 15 mmol kg^{-1}) concentrations are similar to those recorded at the Rainbow field (Ludwig et al., 2006).

3. Experimental

Sampling was carried out by the ROV Victor 6000 during the EXOMAR cruise conducted by IFREMER, France, in summer 2005. Samples were taken at the nose of smokers to avoid seawater contamination. The accuracy of the sampling was guided by real time records of the temperature within the chimneys. Samples of volumes up to 750 mL of hydrothermal fluids were collected in airtight titanium syringes. The choice of titanium prevents any chemical interaction and using airtight bottles ensures the recovery of gases. As soon as the fluids were recovered, pH, H_2S and Cl^- concentrations were measured.

3.1. Sample preparation

Notably, throughout the entire sample processing, all glassware used was combusted at 400 °C for 4 h to remove any trace of organic matter. Organic molecules were extracted from the aqueous matrix and concentrated by means of Stir Bar Sorptive Extraction (SBSE) and Solid Phase Extraction (SPE). The use of two extraction techniques was motivated by two goals: to carry out compound-specific stable carbon isotope measurements and to minimise contamination sources. Isotopic analyses could be achieved on the SPE extract; given the laboratory facilities, isotopic measurements would, however, not have been compatible with the SBSE technique. The SPE technique presented numerous sources of contamination, which could not allow us to confidently discriminate hydrothermally derived compounds from

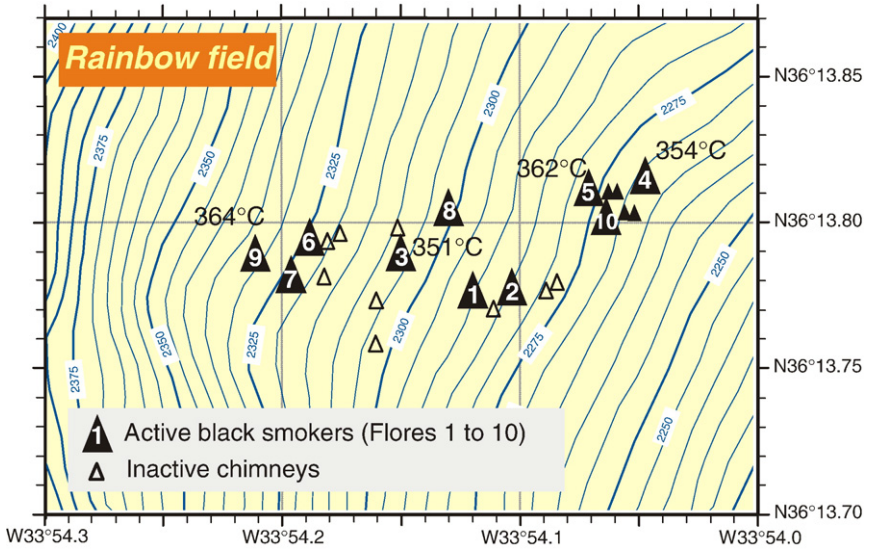

Fig. 2. Location of active black smokers at the Rainbow hydrothermal field. Even though they are spread out, the uniformity of end-member major-, minor-, trace-elements concentrations and gas contents suggests that all Rainbow fluids originate from the same de deep source. From Charlou et al. (2002), Chem. Geol., 191(4), 345–359. The map was established during the FLORES cruise, but the smokers were sampled again during the EXOMAR cruise. Full triangles with numbers correspond to the smokers' location and Table 2 refers to those same numbers.

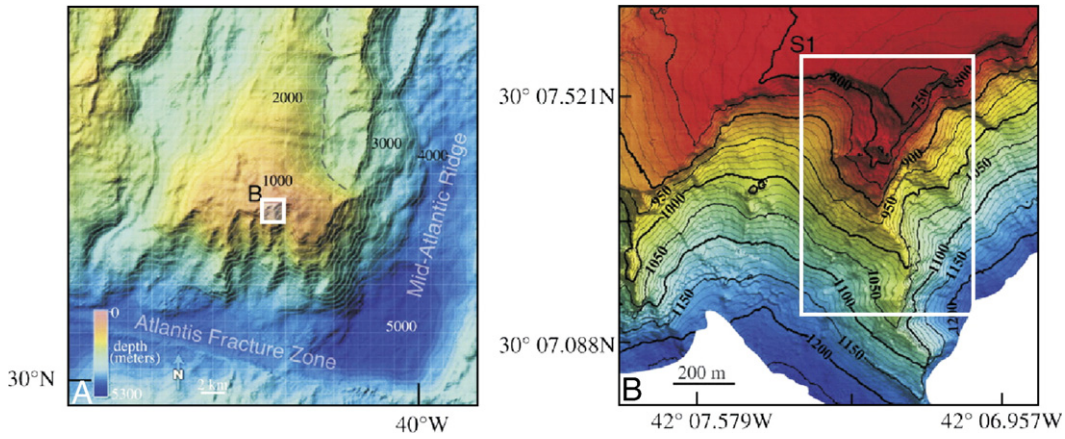

Fig. 3. A. Location map of the Atlantis Massif at 30°N along the Mid-Atlantic Ridge (MAR). The white box indicates the location of the Lost City Hydrothermal Field on the southern ridge of the massif. B. Southern wall of the Atlantis Massif. The white box shows the areal extent of the Lost City vent field, located on a terrace of the southern wall. From Kelley et al. (2005), Science, 307, p 1428.

contaminants; instead the SBSE technique should solve the contamination issue.

The SBSE is a new, convenient and free of contamination technology which allows gas chromatographic analysis of organic compounds from aqueous matrices faster than with conventional techniques, omitting time-costly preparation steps and solvents. The Twister® bars used in this study are magnetic stir bars coated with PolyDiMethylSiloxane. PDMS is a polymer that behaves like a liquid resulting in a classic liquid–liquid extraction that has a reaction constant taken equal to the separation constant of a compound between an octanol and a water phase ($K_{o/w}$); more details on the principle can be found in Baltussen et al. (1999). However, it is much more efficient, requiring minimal sample volumes, quickly reaching equilibrium, being 1000 times more sensitive than SPME and giving 100% recovery. Just before use, Twisters® were conditioned, i.e. cleaned by thermal desorption, on board at 300 °C for 4 h under a purified helium flow (50 mL min^{-1}) (Fig. 4). 10 mL aliquots of hydrothermal fluids samples were transferred from the titanium syringes into glass vials where the clean Twisters® were introduced and left to stir for 60 min. The Twisters® were then removed, allowed to dry and stored in their glass vials under helium until analysis by Thermal Desorption–Gas Chromatography–Mass Spectrometry (TD–GC–MS).

The SPE technique relies on the adsorption of organic compounds on a reversed phase, for which a hydrophilic–lipophilic-balanced water-wettable co-polymer was selected in our study (single-use Oasis® HLB cartridges, *Waters Corporation*). The sorbent was activated first with 1 mL acetonitrile (*Riedel*) and 5 mL methanol (*Riedel*) and then equilibrated with 5 mL of Milli-Q water. A 50 mL aliquot of fluid was collected in Duran glass vials, and filtered through 0.45 μm filters. These filtrates were slowly flushed through Oasis® HLB cartridges using the positive pressure of a syringe. Impurities were flushed away with 5 mL Milli-Q water and the sorbent was dried by pushing air with a syringe. Cartridges were stored at +4 °C until elution in the geochemistry laboratory at IFREMER, Brest, France. Three successive elutions were performed: 0.5 mL of hexane (*Riedel*) to release polar to mid-polar compounds, 0.5 mL of methanol (*Riedel*) to extract polar compounds and 0.5 mL of dichloromethane (DCM) (*Riedel*) to check if any other compounds were recovered. Each fraction was collected in 1.5 mL Gas Chromatography (GC) glass vials, and analysed immediately by Gas Chromatography–Mass Spectrometry (GC–MS).

3.2. Blank experiments

Deep seawater was sampled away from the hydrothermal system to avoid contamination by the latter, but still close enough to be relevant to the actual area of study. Samples were collected, processed and analysed according to the same protocols used for the hydrothermal fluid samples.

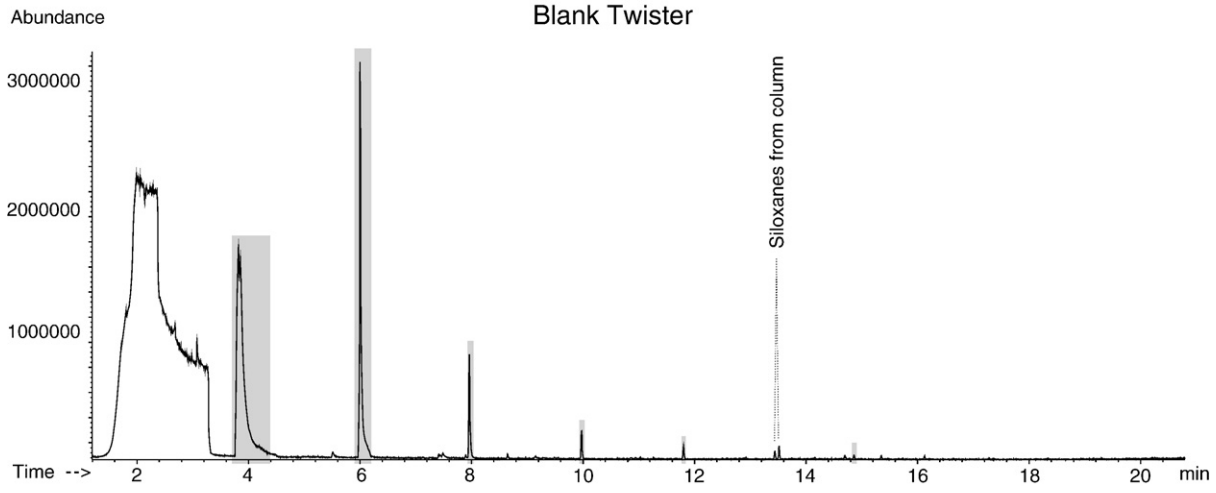

Fig. 4. GC–MS Total Ion Current (TIC) trace signature generated by a Twister after conditioning at 300 °C for 4 h under 50 mL min^{-1} purified helium flow. It consists in 6 compounds, all being siloxanes, whose retention times are 3.86, 6.00, 7.96, 9.98, 11.80, 13.44 and 14.86 min. The corresponding peaks are highlighted in grey.

A problem that remains is that of the potential effect of H_2S, high chlorinity and pH on PDMS, the SPE phase, the cartridge itself and the filters. The various polymers present in these accessories may indeed release some compounds when exposed to H_2S, chlorinated solutions and extreme pH. In order to evaluate the extent to which organic contaminants may have interfered with the samples, 4 solutions mimicking hydrothermal fluids (referred to as A1, B1, N1 and B3 in Table 1), in terms of pH, chlorinity and H_2S contents, were prepared on-shore and treated as natural samples. Various amounts of NaCl and $Na_2S{\cdot}9H_2O$ (*98+% A.C.S reagent, Aldrich*) were added to MilliQ water and pH was adjusted by addition of NaOH or HCl. The H_2S and Cl^- concentrations were then measured by the same titration methods as used on board, and pH was measured using a pH/millivolt-meter (*METROHM*) (Table 1). Following the same procedure as the one used for the natural samples, 50 mL aliquots of these solutions were conditioned on Oasis® HLB cartridges (*Waters Corporation*), which were eluted and the extracts analysed by GC–MS. In the same manner Twisters® were stirred in 10 mL of each solution and analysed by TD–GC–MS.

3.3. Thermal Desorption–Gas Chromatography–Mass Spectrometry (GC–MS)

The Twisters® were thermally desorbed in the Thermal Desorption System TDS-2 (*GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany*) mounted on a 6890 Agilent GC (*Agilent Technologies, Little Falls, DE, USA*) equipped with a 5973 quadrupole mass spectrometer detector (MSD). The TDS was coupled to a Cooled Injection System CIS3 (*GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany*), that mates the injection liner of the GC–MS, for cryofocusing of the analytes prior transfer into the analytical column. Liquid nitrogen was used to cool down and maintain the CIS at −196 °C while the Twister was being desorbed at 300 °C under helium flow in the TDS. The CIS was then heated at a temperature of 250 °C. Separation was achieved on an HP5-MS capillary column (30 m×0.25 mm i.d.×0.25 μm film thickness). The GC operating conditions were as follows: temperature held first at 40 °C for 1 min, ramp from 40 to 320 °C at 12 °C min^{-1} and held at 320 °C for 2 min. Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}. The mass spectrometer was operated in electron impact (EI) mode at 70 eV ionization energy and scanned from 10 to 500 Da. Data were acquired and processed by Chemstation software. Individual compounds were identified by comparison of recorded mass spectra with library (NIST02) data.

3.4. Gas Chromatography–Mass Spectrometry (GC–MS)

The SPE fluids extracts were analysed by GC–MS on a 6890 Agilent GC (*Agilent Technologies, Little Falls, DE, USA*) equipped with a 5973 quadrupole mass spectrometer detector (MSD). The injector was used in splitless mode at a temperature of 250 °C. Separation was achieved on an HP5-MS capillary column (30 m×0.25 mm i.d.×0.25 μm film thickness). The GC operating conditions were as follows: temperature held first at 40 °C for 6 min, ramp from 40 to 85 °C at 2 °C min^{-1}, ramp from 85 to 210 °C at 10 °C min^{-1}, ramp from 210 to 300 °C at 20 °C min^{-1} and held at 320 °C for 2 min. Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV ionization energy and scanned from 10 to 500 Da. Data were acquired and processed by Chemstation software. Individual compounds were identified by comparison of recorded mass spectra with library (NIST02) data.

Table 1
pH, Cl and H_2S contents of the four artificial hydrothermal solutions

Solution	pH	H_2S (mmol kg^{-1})	Cl (mmol kg^{-1})
A1	3.13	0	305
B1	11.35	0.13	544
N1	5.46	0.41	835
B3	11.86	3.3	5

3.5. Gas Chromatography–Isotope Ratio Mass Spectrometry (GC–IRMS)

The hexane, methanol and DCM extracts were reduced to one third of their volume by evaporation at room temperature under gentle N_2 flow prior to further analyses. These concentrated extracts were injected automatically in a Thermo GC/C system, consisting of an HP 6890 GC coupled to a Thermo Delta +XL IRMS. Separation was achieved on an HP5-MS capillary column (30 m×0.25 mm i.d.×0.25 μm film thickness), and chromatographic conditions identical to those used for the GC–MS analyses were applied here to obtain similar chromatography. After separation, all compounds were converted to CO_2 (and H_2O), and the carbon isotopic composition of individual compounds was measured. The usual $\delta^{13}C$ was used to express the results, and values are reported relative to the conventional V-PDB limestone standard. Typical reproducibility for $\delta^{13}C$ measurements on well-resolved peaks with sufficient peak intensity is estimated to be ±0.5‰ or better.

4. Results

Based on the pH, temperature, Cl^- and Mg concentrations, only close to end-member hydrothermal fluids (i.e. very little mixing with surrounding deep seawater) were selected for analyses. Several samples of each hydrothermal field from different vents were analysed and proved to be consistent. Fig. 5 shows an example of five overlaid chromatograms obtained for Rainbow and Lost City and Table 2 gives the major characteristics of these ten different samples. Similar patterns were observed although chromatograms differed only for a few peaks and in abundances. These minor variations observed in the organic content are most likely related to the vents which certainly expel at different flows and have different chemistries of chimneys. In addition, the mix ratio with seawater, which appears in the pH value and the concentrations of H_2S and Cl^-, might also influence the organic content. Two representative samples (TW8 and TW34) were selected and studied in detail for this work. We wish to point out that our data are only qualitative; and hence abundances will not be discussed. Instead we will present here an overview of the organic compounds identified in the fluids.

4.1. Blanks

Fig. 4 shows the characteristic Total Ion Current (TIC) of a conditioned Twister. The six peaks that arise at 3.86, 6.00, 7.96, 9.98, 11.80, 13.44 and 14.86 min are the signature of the PDMS coating. They appear in all TIC obtained with the Twister extracts and were therefore highlighted in grey on all TIC to be used as internal landmarks. Except from those particular peaks and some other siloxanes from the capillary column, the rest of the TIC is only background noise, which demonstrates the cleanliness of the method.

Organic compounds occurred in very low concentration in the deep seawater sample treated with SPE. Only a few peaks appeared between 9.5 and 40 min but their abundances were far smaller than the ones at Lost City and Rainbow (f and g on Fig. 6). By contrast the use of SBSE technique, which is much more sensitive, revealed the presence of compounds in the deep seawater sample. However, the TIC trace of the deep seawater extract revealed that no compound occurred in the 4 to 8 min zone whereas, in that zone, the Lost City and Rainbow TIC traces showed a large amount of peaks. This undeniable enrichment in organic compounds of hydrothermal fluids is highlighted by Fig. 7. As for compounds occurring after 8 min in the deep seawater extract most of them were biologically related compounds such as ketones, aldehydes, alcohols and N, P, S bearing compounds.

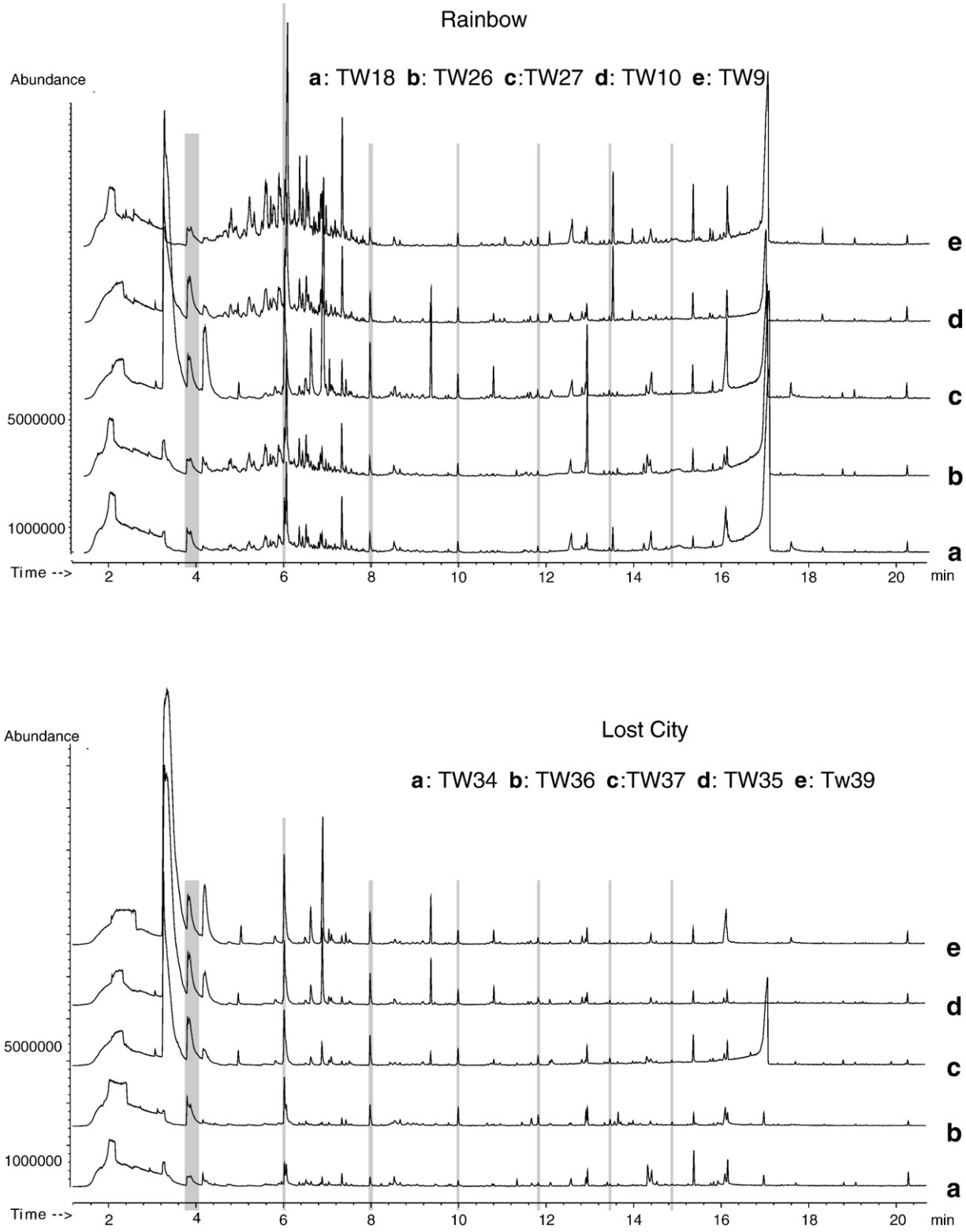

Fig. 5. Overlaid TIC chromatograms obtained after Twister extraction of 5 different samples from 5 different vents for both Rainbow (top) and Lost City (bottom) hydrothermal fields. These chromatograms revealed good consistency within one field.

Some of them were detected in the hot fluids extracts but in much lower concentrations.

Our artificial hydrothermal fluids definitely affected the SPE phases and resulted in the leaching of various compounds. Indeed, TIC traces revealed more contaminants (a–d on Fig. 6) which were distributed at the beginning and the end of the chromatograms, thus leaving the 9.5 min–40 min region relatively clean. Among the 4 solutions, B3 showed the largest number of compounds in the hexane extract whereas A1 showed the largest number in the MeOH extract. On the contrary the synthetic hydrothermal solutions did not seem to significantly alter the PDMS phase of the stir bars (Fig. 8). Twisters® that were stirred in high pH solutions (B1 and B3) showed increased

Table 2
Features of the ten samples used in this work

Field	Sample	Location	Depth (m)	T (°C)	pH	H_2S	Cl^-	Mg^{2+}
Rainbow	TW9	8	2306	353	3.74	1.3	772	5.0
Rainbow	TW10	3	2306	353	3.79	0.96	774	5.7
Rainbow	TW18	9	2307	359	3.57	0.93	783	3.2
Rainbow	TW26	7	2293	324	3.40	1.5	769	4.9
Rainbow	TW27	6	2293	324	3.43	1.4	767	4.8
Lost City	TW34	EXO11	741	94	11.57	0.12	537	1.0
Lost City	TW35	EXO11	748	93	11.72	0.21	556	0.8
Lost City	TW36	Flange 2M	773	64	10.02	0.49	570	39.9
Lost City	TW37	Flange 2M	772	64	9.94	0.53	569	37.1
Lost City	TW39	EXO12	781	90	10.75	0.36	545	12.3

Concentrations are given in mmol kg^{-1}. Data were acquired on board during the EXOMAR cruise. For the Rainbow site, location is referred to a number which corresponds to the smoker's number on Fig. 2.

signals for silanes and siloxanes, whereas those stirred in more or less acidic solutions (A1 and N1) seemed to leach phtalates. Besides those large peaks, a few small peaks appeared in the different chromatograms but none corresponded to any of the compound discussed in the present paper. They were all more complex and heavier molecules.

4.2. Organic contents of the hydrothermal fluids

Screening of all the chromatograms enabled discrimination between contaminants and hydrothermally derived compounds. Contaminants appeared in most cases to belong to specific groups of compounds and thus these whole groups were discarded. The remaining groups were hydrocarbons, aromatic hydrocarbons and linear carboxylic acids. Only a few compounds belonging to these groups were detected in the blanks. Full details are presented in Table 3 and Fig. 9 illustrates the distribution of the compounds in the chromatograms. Most of the compounds occurred in both SPE and SBSE extracts and almost all the ones detected in the hydrothermal fluids extract were absent in the deep seawater. An interesting point is that of all the compounds but four occurring in the fluids extracts were low molecular weight molecules (≤C15), contrary to most of the pollutants (>C15) commonly found when dealing with marine samples (Grosjean and Logan, 2007). In addition, the general trend is the dominance of the heavier molecules in the control and blank extracts, which support the assumption that they are contaminants. Among the compounds listed in Table 3, the one occurring both in the fluids and in the blanks, or only present in the SPE extracts, will not be discussed as they would need further investigation to be proven native of the fluids.

4.2.1. Hydrocarbons

Hydrocarbons were by far the most numerous compounds spotted in the fluids and their chain length ranged from C9 to C18. The fluids contained a mix of even and odd carbon numbered compounds and there were no indications for a carbon preference. They consist of four main groups: n-alkanes (C9 to C14) which have been reported

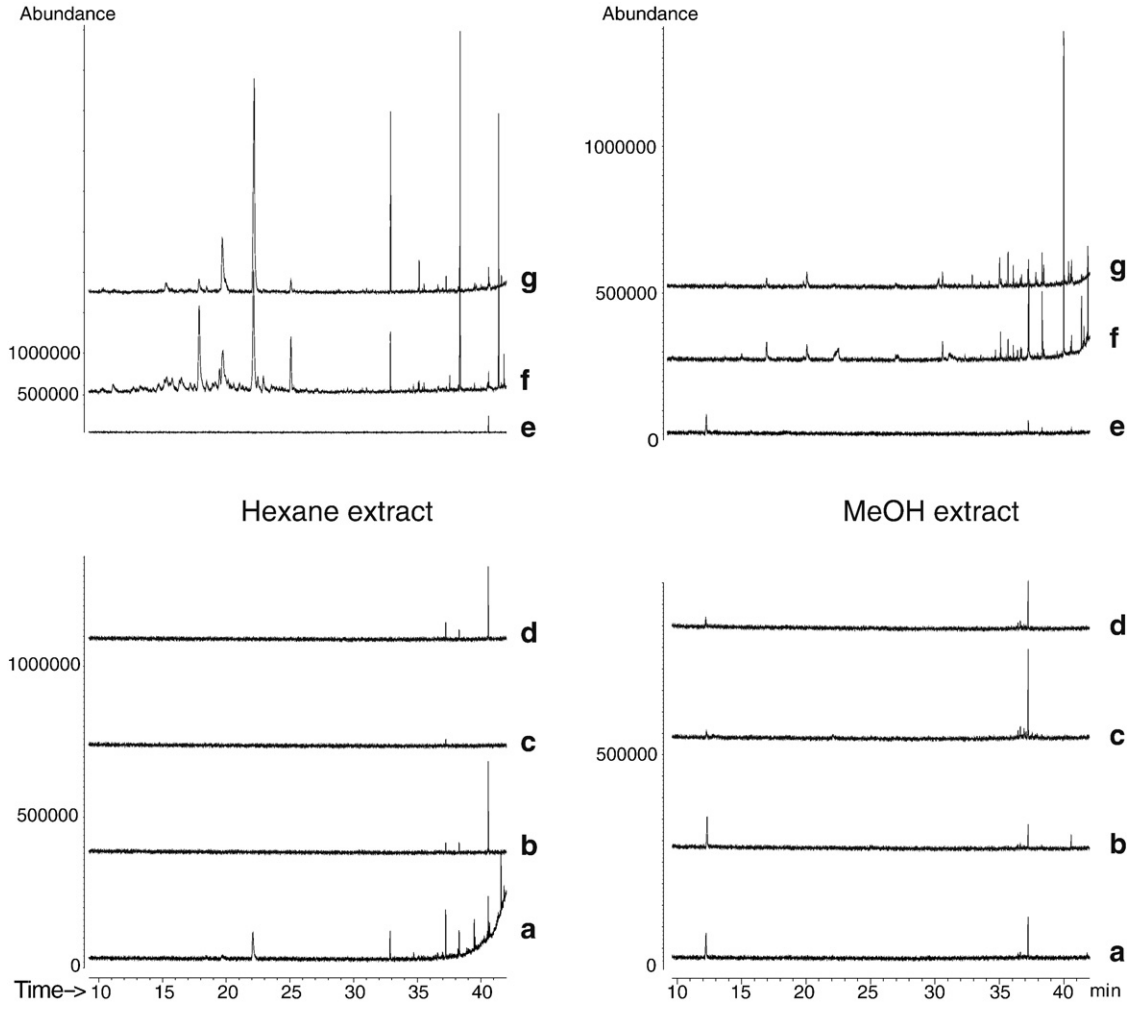

Fig. 6. Overlaid TIC Chromatograms of hydrothermal fluids extracts, deep seawater extracts and fake hydrothermal solutions extracts (a to d). TIC of hexane extracts are shown on the left and TIC of MeOH extracts on the right. a: B3, b: N1, c: A1, d: B1, e: Seawater, f: Rainbow, g: Lost City.

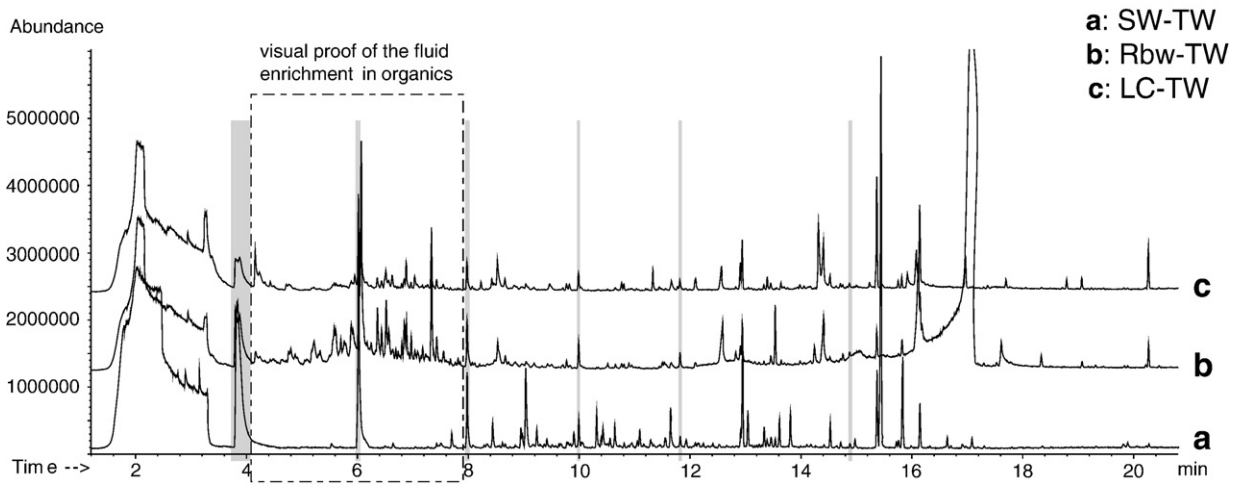

Fig. 7. GC–MS Total Ion Current (TIC) traces obtained after Twister extraction. Overlay of: a: deep seawater, b: Rainbow, c: Lost City. The 4 to 8 min zone shows the obvious enrichment in organic molecules of the Rainbow and Lost City hydrothermal fluids. In grey are the characteristic Twister's peaks.

previously by Holm and Charlou (2001), branched alkanes (C9 to C12) and cycloalkanes (C9 to C11). Branched alkanes have several chain isomers which show similar mass fragmentograms so that they cannot be identified without co-elution with a standard. Therefore they were referred only to their molecular formula. Cycloalkanes were mostly cyclohexanes with a maximum side chain length of 6 carbon atoms, the remaining being cyclopentane and hydrogenated naphthalene. Chain isomers could not be confidently identified either without a standard and therefore the side chain(s) position(s) was (were) left as question marks.

4.2.2. Aromatics

Toluene was clearly identified as well as phenol. Branched benzenes (C9 to C12) were observed but were not named as chain isomers have similar fragmentograms. Therefore they are listed according to their molecular formula. Bicyclic aromatic compounds, namely naphthalene (or azulene which have almost the same fragmentation pattern) and branched naphthalene (C11–C12) were also detected. Finally, Polycyclic Aromatic Hydrocarbons (PAH) of 3 or 4 cycles were clearly evidenced by the SBSE technique but not by SPE, which is likely due to higher limit of detection and lower recovery rates reached by the SPE method (Baltussen, 1999).

4.2.3. Organic acids and methyl esters

N-alkanoic acids (C9 to C18) were clearly evidenced in the SBSE extracts. Whereas only a few alkanoic acids were showing very weak signal and could be detected by SPE, the peaks obtained by SBSE are high and well resolved thanks to the high sensitivity of the method. As with hydrocarbons, carbon preference was absent for this group of compounds.

4.3. Rainbow vs. Lost City

Considering the very distinct inorganic characteristics of the two fluids, we expected variations in their organic composition. However, very little difference was observed, as could be seen on Fig. 9. The same groups of compounds were detected in both fluid types, but variations within groups of compounds can be noted (Table 3). A general trend is the presence of more aromatic compounds in the Lost City fluids compared to the Rainbow fluids.

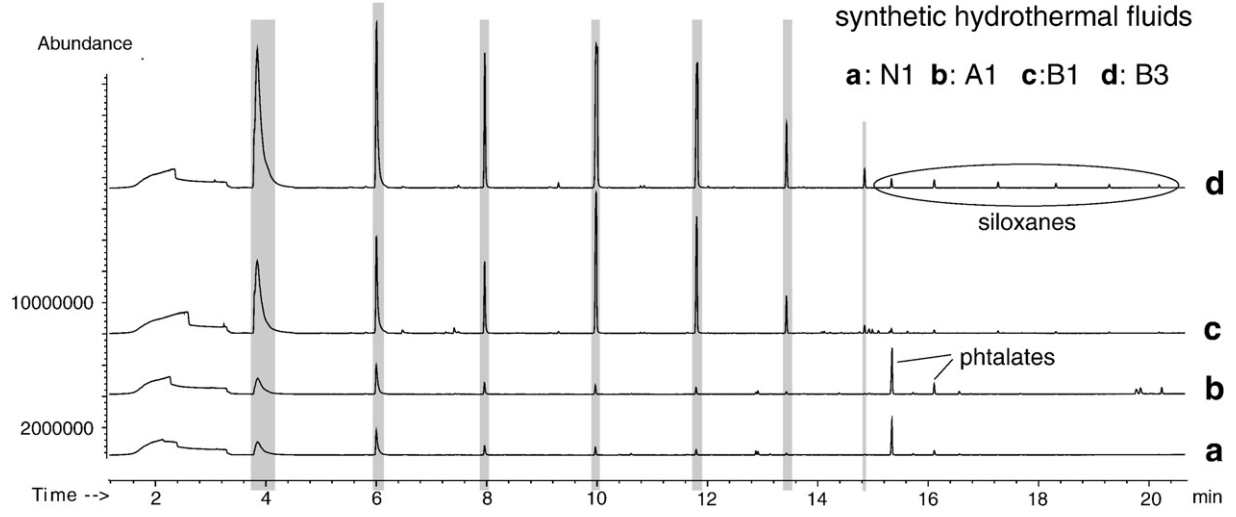

Fig. 8. Overlayed TIC Chromatograms of stir bars treated with artificial hydrothermal solutions.

Table 3
Organic compounds detected in, left to right: deep seawater, Rainbow and Lost City SBSE extracts and Rainbow, Lost City, deep seawater, artificial hydrothermal fluids (A1, B1, N1, B3) SPE extracts

Compounds	Formula	SW-TW	Rbw-TW	LC-TW	Rbw-SPE	LC-SPE	SW-SPE	A1	B1	N1	B3
n-alkanes											
Heptane	C7H16	nd	nd	nd	nd	nd	x	nd	x	x	x
Nonane	C9H20	nd	x	x	x	x	nd	nd	nd	nd	nd
Decane	C10H22	nd	x	x	x	x	nd	nd	nd	nd	nd
Undecane	C11H24	x	x	x	x	x	x	x	x	x	x
Dodecane	C12H26	nd	x	x	x	x	nd	nd	nd	nd	nd
Tridecane	C13H28	nd	x	x	x	x	nd	nd	nd	nd	nd
Tetradecane	C14H30	nd	x	x	x	x	nd	nd	x	nd	x
Pentadecane	C15H32	nd	nd	nd	?	x	nd	nd	nd	nd	x
Hexadecane	C16H34	nd	nd	nd	x	x	x	x	x	x	x
Heptadecane	C17H36	nd	nd	nd	x	x	nd	nd	nd	nd	x
Octadecane	C18H38	nd	nd	nd	x	x	x	nd	x	x	x
Nonadecane	C19H40	x	x	x	x	x	nd	nd	nd	nd	x
Eicosane	C20H42	nd	?	?	x	x	x	nd	x	x	x
Branched alkanes											
	C9H20	nd	x	x	nd	nd	nd	nd	nd	nd	nd
	C10H22	nd	xx	xx	xxxxxx	xxx?	nd	nd	nd	nd	nd
	C11H24	nd	xxxxx	xxxx	xxxx	xxx	nd	nd	nd	nd	nd
	C12H26	nd	x	nd	xxxxx	xxx	nd	nd	nd	nd	nd
	C13H28	nd	x	nd	x	?	nd	xx	nd	nd	x
	C15H32	nd	nd	nd	nd	nd	nd	nd	nd	nd	x
	C16H34	nd	nd	nd	nd	x	nd	nd	x	nd	nd
	C16–18	nd	nd	nd	nd	x	nd	x	x	x	x
	C18H38	nd	nd	x	nd	nd	x	x	x	x	nd
	C19H40	nd	nd	nd	nd	nd	nd	nd	nd	nd	x
	C20H42	nd	nd	nd	nd	nd	nd	x	nd	nd	x
Cycloalkanes											
Cyclohexane, 1,?,? -trimethyl	C9H18	nd	xx	xx	x	nd	nd	nd	nd	nd	nd
Cyclohexane, 1-ethyl, ?-methyl	C9H18	nd	xx	xx	xx	?	nd	nd	nd	nd	nd
Cyclohexane, -propyl	C9H18	nd	x	x	x	x	nd	nd	nd	nd	nd
Naphtalene, decahydro-, trans	C10H18	nd	x	x	x	x	nd	nd	nd	nd	nd
Cyclohexane, 1-methyl, ?-propyl	C10H20	nd	xxx	xxx	xx	xx	nd	nd	nd	nd	nd
Cyclohexane, butyl-	C10H20	nd	x	x	x	nd	nd	nd	nd	nd	nd
Cyclohexane, 1-ethyl-2,3-dimethyl-	C10H20	nd	x	x	nd	nd	nd	nd	nd	nd	nd
Cyclohexane, 1-methylbutyl	C11H22	nd	nd	nd	x	nd	nd	nd	nd	nd	nd
Naphthalene, decahydro-2-methyl-	C11H22	nd	nd	nd	x	x	nd	nd	nd	nd	nd
Cyclohexane, pentyl-	C11H22	nd	x	x	x	x	nd	nd	nd	nd	nd
Cyclopentane, hexyl-	C11H22	nd	x	x	x	x	nd	nd	nd	nd	nd
Cyclohexane, 1,2-diethyl-1-methyl-	C11H22	x	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cyclohexane, hexyl-	C16H32	nd	nd	nd	x	x	nd	nd	nd	nd	nd
Cyclohexane, decyl-	C16H32	nd	nd	nd	x	?	nd	nd	nd	nd	nd
Aromatics											
Monocyclic											
Phenol	C6H6O	nd	x	x	x	x	nd	nd	nd	nd	nd
Toluene	C7H8	nd	x	x	x	x	x	x	x	x	x
Styrene	C8H8	nd	x	x	x	x	x	nd	nd	nd	nd
Benzene, alkyl	C8H10	x	xx	xx	x	x	nd	nd	nd	nd	nd
Benzene, alkyl	C9H12	nd	nd	xx	x	xx	nd	nd	nd	nd	nd
Benzene, alkyl	C10H14	nd	nd	xx	nd	nd	nd	nd	nd	nd	nd
Benzene, alkyl	C12H18	nd	x	x	xx	nd	nd	nd	nd	nd	nd
Bicyclic											
Naphtalene/azulene	C10H8	x	x	x	xx	xx	nd	nd	nd	nd	nd
Naphtalene, alkyl	C11H10	nd	x	xx	nd	nd	nd	nd	nd	nd	nd
Naphtalene, alkyl	C12H12	nd	nd	xxxxx	nd	nd	nd	nd	nd	nd	nd
Naphtalene, alkyl	C13H12	nd	nd	x	nd	nd	nd	nd	nd	nd	nd
PAH											
Acenaphthene	C12H10	nd	nd	x	nd	nd	nd	nd	nd	nd	nd
Fluorene	C13H10	nd	x	x	nd	nd	nd	nd	nd	nd	nd
Phenanthrene/anthracene	C14H10	nd	x	x	nd	nd	nd	nd	nd	nd	nd
Pyrene	C16H10	nd	x	nd	nd	nd	nd	nd	nd	nd	nd
n-alkanoic acids											
Nonanoic acid	C9H18O2	nd	x	nd	x	nd	x	x	nd	nd	nd
Decanoic acid	C10H20O2	nd	x	x	nd	x	nd	nd	nd	nd	nd
Dodecanoic acid	C12H24O2	nd	x	x	nd	x	nd	nd	nd	nd	nd
Tetradecanoic acid	C14H28O2	nd	x	x	nd	nd	x	nd	nd	nd	nd
Pentadecanoic acid	C15H30O2	nd	x	x	nd	nd	nd	nd	nd	nd	nd
Hexadecanoic acid	C16H32O2	nd	x	x	nd	nd	x	x	nd	nd	nd
Octadecanoic acid	C18H36O2	nd	x	nd	nd	nd	x	x	nd	nd	nd

The number of cross stands for the number of times the compound has been detected. Question marks are used in case of very weak signal or uncertainty. Non detected compounds are referred to nd. Chain position numbers were left as question mark in compounds names when chain isomers could not be differentiate. The isomers Naphthalene and Azulene as well as Phenanthrene and Anthracene have similar fragmentograms and thus could not be differentiate either.

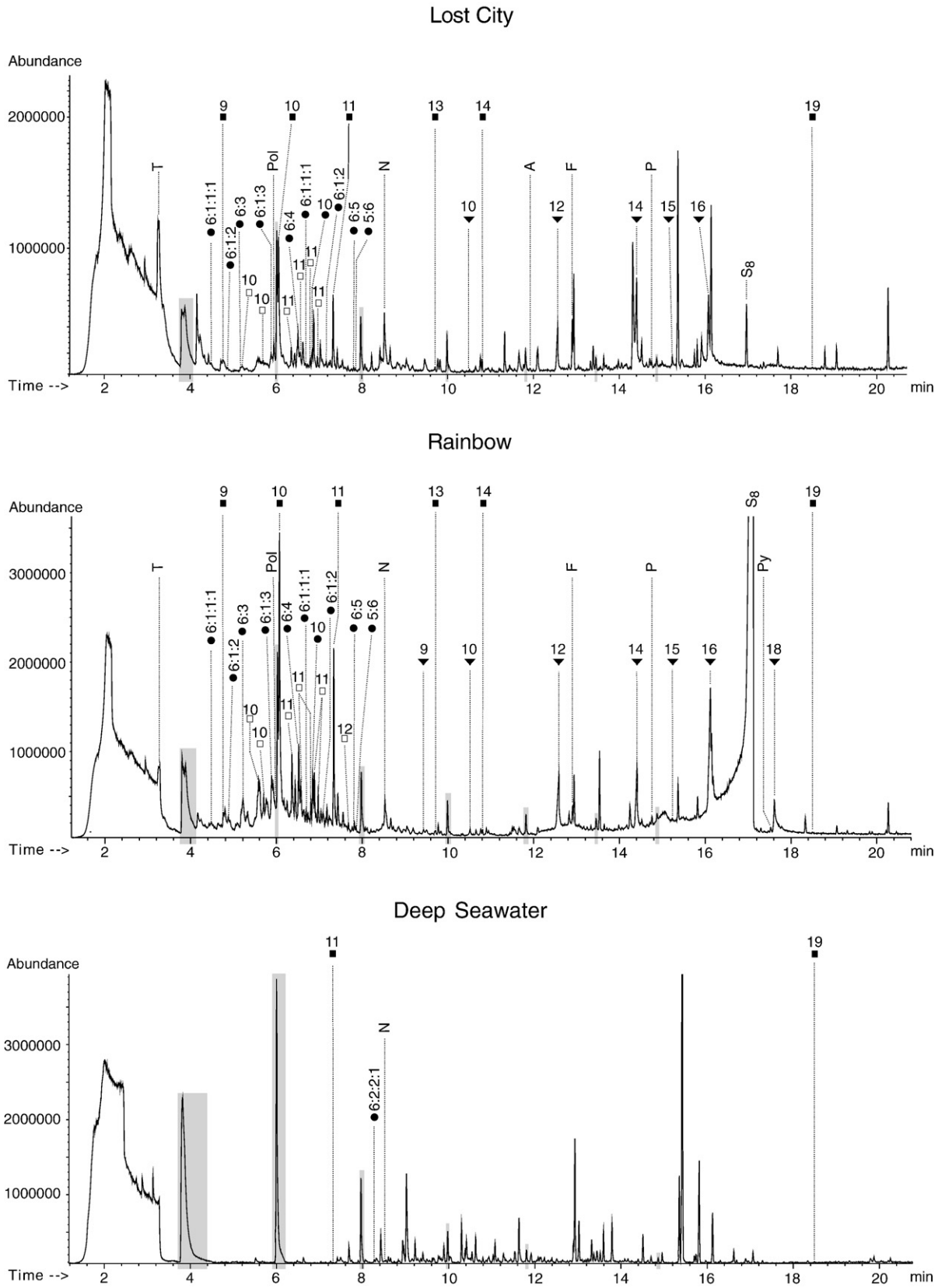

Fig. 9. GC–MS Total Ion Currents (TIC) traces of the Twister extracts for the Lost City and Rainbow fields and the deep seawater reference. Numbers stand for the total number of carbon for n-alkanes (full squares), branched alkanes (empty squares) and carboxylic acids (full triangles). Cycloalkanes (full circles) are distinguished by the number of carbon in the cycle (first figure) and the number of carbon of the side chains (following figures). T, N, P, Py, A and Pol are short for Toluene, Naphtalene, Phenanthrene, Pyrene, Acenaphtene and Phenol. Cyclooctaatomic sulfur (S8) was added because the peak was major on the Lost City TIC and for consistency on the Rainbow TIC. In grey are the characteristic Twister's peaks.

Table 4
Isotopic composition of n-alkanes and carboxylic acids present in Rainbow and Lost City hydrothermal fluids

Compound	Formula	δ^{13}C (‰)	
		Rainbow	Lost City
Nonane	C9H20	−45.9	−27.3
Decane	C10H22	−37.1	−40.8
Undecane	C11H24	−40.3	−45.8
Dodecane	C12H26	−39.9	−26.7
Tetradecane	C14H30	−29.9	–
Octanoic acid	C8H16O2	–	−31.1
Decanoic acid	C10H20O2	–	−19.6
Dodecanoic acid	C12H24O2	–	−25.8

4.4. Carbon isotopic composition

Because of the large number of compounds present in the fluids and their very low concentration, insufficient resolution of the majority of the peaks and only very weak GC signals could be obtained. Thus δ^{13}C could only be accurately measured for a few compounds. As most published data deal with hydrocarbons, which may be in close relationship with carboxylic acids, we decided to focus on these two groups.

The compounds detected in our samples showed a δ^{13}C value in the −46 to −20‰ range (Table 4). The variation of δ^{13}C of the n-alkanes with respect to carbon number (Fig. 10) showed a positive trend in the Rainbow fluids, whereas no clear pattern could be identified in data from the Lost City fluids. We were not able to obtain reliable δ^{13}C value for carboxylic acids in the Rainbow fluids because of their low concentrations. Little data is presented here; however, it seemed that n-alkanoic acids were more enriched in ^{13}C vs. n-alkanes of the same chain length (Table 4 and Fig. 10).

5. Discussion

Before discussing the composition of organic compounds in our hydrothermal fluid samples, it should be mentioned that Low Molecular Weight (LMW) compounds are most likely too volatile to be detected by our chromatographic settings. As for the heavier (HMW, high molecular weight) compounds, the end of the chromatogram where they would elute was often difficult to interpret due to high backgrounds. Therefore, we do not reject the occurrence of LMW and HMW compounds in hydrothermal fluid samples, but assume that our analytical approach is not suitable for the detection and identification of these groups of compounds. We will discuss the presence and the origin of the various compounds evidenced in the hydrothermal fluids, with the support of field data from earlier studies, thermodynamics, results of laboratory experiments and carbon isotopic ratios.

5.1. Fluids vs. rocks

In 1994, Sugisaki and Mimura (1994) reported the occurrence of saturated alkanes (C14 to C33) and possibly cycloalkanes in mantle-derived rocks. They argued for a mixed origin consisting of hydrocarbons that had been preserved in the mantle, recycled biogenic hydrocarbons, and abiogenic compounds. Consistent with this, recent studies on organic compounds in serpentinites from the Lost City hydrothermal system have revealed the presence of high abundances of n-alkanes C15 to C30 (Delacour et al., 2007, 2008). The authors explained that the high fluid fluxes in the basement rocks beneath the field likely favoured the transport and incorporation of marine dissolved organic carbon into the serpentinites. Thus, although a biogenic origin would be consistent with these findings, no firm case can be made either way. Therefore, the authors did not disregard the possibility of an abiogenic origin. Indeed, a comment (Kenney, 1995) on Sugisaki's work (Sugisaki and Mimura, 1994) strongly supported the abiotic origin of mantle hydrocarbons. In addition, isoprenoids, steranes and hopanes could not be detected in hydrothermal fluids, which would support the abiogenic origin of the lighter hydrocarbons (<C14) present in the fluids. However, the heavier compounds may not have been detected in our samples, either because their solubility in the circulating fluids may be too low, or, on the contrary, because they were dissolved at some stage but were subsequently cracked at higher pressure and temperature deeper in the mantle; resulting in the lighter molecules observed.

5.2. Fluids vs. sulfide deposits

In their study of the sulfide deposits at the Rainbow field, Simoneit et al. (2004) reported a great variety of organic molecules. All groups of compounds detected in the hydrothermal fluids in the present study also occurred in the sulfide deposits studied by Simoneit and co-workers. The major difference that stands out is the clear dominance of heavy molecular weight molecules in the deposits, with hydrocarbons mostly in the C14–C39 range and fatty acids in the C12–C25 range. Both were interpreted as the result of thermal degradation of autochthonous microbial communities. Whether the shorter molecules identified in our fluid samples are abiogenic or fragments from thermogenesis of heavier biogenic molecules remains to be clarified.

In the same manner, branched cyclohexylalkanes and cyclopentylalkanes showed much longer side chains in the sulfide deposits analysed by Simoneit et al. (2004); C8 to C24, in contrast to a maximum of 6 carbons for hydrothermal fluids in this study. The authors did not

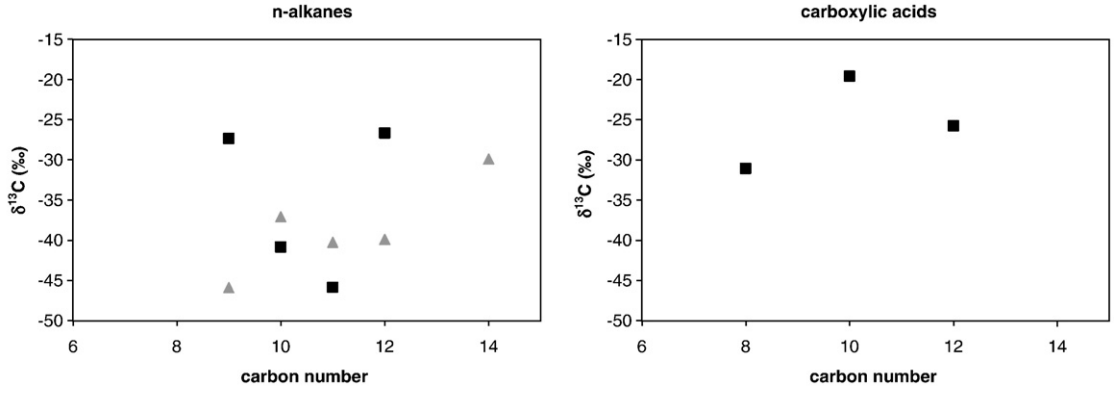

Fig. 10. Isotopic composition vs. carbon number of n-alkanes (left) and carboxylic acids (right) recorded in Rainbow (triangles) and Lost City (squares) hydrothermal fluids. Carboxylic acids in Rainbow fluids showed a signal too weak for reliable δ^{13}C measurements.

provide any explanation for their occurrence in the sulfide deposits, neither do we have an interpretation for the light ones found in the fluids, apart from the fact that they are not contamination according to Grosjean and Logan (2007).

Within the branched alkane group, only gemdialkyl alkanes and methyl alkanes were identified in the sulfide deposits studied by Simoneit et al. (2004). In our case, branched alkanes were also detected but the absence of appropriate standards precluded identification and they are not discussed further.

Finally, aromatic molecules have not been detected in the sulfide deposits (Simoneit et al., 2004), presumable because of their high solubility in the fluids and their consequent removal from the hydrothermal system by fluid flow (Kawka and Simoneit, 1990). The presence of toluene, branched benzenes and PAH in the fluids is thus consistent.

5.3. Nature vs. theory

Could the organic compounds in hydrothermal fluids be abiotic, i.e. are there purely geochemical reactions that could produce them? A prerequisite for chemistry to occur is that the reactions are thermodynamically favourable. As mentioned in the introduction, metastable intermediates in the form of organic compounds are likely to be synthesised in hydrothermal systems due to kinetic barriers that would prevent the stable equilibria CH_4/CO_2 and NH_3/N_2 to establish. These intermediates would be stabilised provided fH_2 is high enough (Shock, 1990, 1992) (Fig. 11). fH_2, which is buffered by the mineral assemblage of the system, is thus crucial for the persistence of organic molecules in hydrothermal fluids. The PPM (pyrite–pyrrhotite–magnetite) and FMQ (fayalite–magnetite–quartz) assemblages have been used for describing fH_2 in basaltic systems but to the best of our knowledge there is no consensus for ultramafic-hosted systems, i.e. no model for the upper mantle buffer. This is probably due to the complexity of the mineral composition and the various alteration processes occurring in these systems. Indeed Frost and Beard (2007) tackled the intricacies and variability of buffering in serpentinised ultramafic rocks. Moreover, the latter study was carried out on the only >1 km cores from ultramafic-hosted hydrothermal fields, which illustrate the lack of samples from a sufficient depth that would enable better comprehension of the upper mantle buffering. However, in order to assess in which domain Rainbow and Lost City were situated, $\log fH_2$ was calculated for both sites using SUPCRT92 (Johnson et al., 1992) software, based on the hydrogen concentrations of the end-member fluids (Kelley et al., 2001; Charlou et al., 2002). The fH_2 calculated values should be considered as approximate values, as it was assumed that molalities were equal to activities. Pressures are 230 bar at Rainbow and 70 bar at Lost City. The values are $\log fH_{2\text{-Rainbow}}$ (230 bar, 350 °C) = 0.34 and $\log fH_{2\text{-LostCity}}$ (70 bar, 100 °C) = 1.34 and are plotted on (Fig. 11).

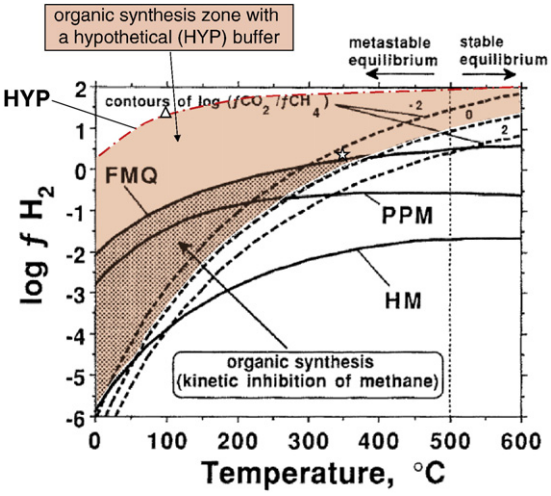

Fig. 11. Modified after Shock (1990). Plot of log fH_2 against temperature. Solid curves show values of log fH_2 buffered by the FMQ, PPM and HM mineral assemblages as functions of temperature. Dashed curves correspond to contours of $\log(fCO_2/fCH_4)$ equal to 2, 0 and −2 as function of temperature. The long dash dot line is a schematic representation, for ultramafic-hosted hydrothermal systems, of log fH_2 buffered by an unknown mineral assemblage (HYP). Dotted vertical line at 500 °C separates range of temperatures where stable equilibrium in the C–H–O system is attained in submarine hydrothermal systems (T>500(C), at which CO_2 reduction to CH_4 is kinetically inhibited, and where metastable equilibrium states between CO_2 and aqueous organic compounds may prevail. Corresponds to the region where synthesis of aqueous organic compounds in metastable states may be most easily detected. Plain light grey area represents the extended stippled area in the hypothetical HYP buffering. The star and the triangle stand for Rainbow and Lost City fluids respectively.

The H_2 fugacity values suggest that the PPM assemblage may not buffer fH_2 at the Lost City and Rainbow vent fields. In contrast, the FMQ buffer might be a correct model for Rainbow, which, in addition, seems to fall into the metastable equilibrium domain that would support the possible formation of organic molecules from oxidized carbon and nitrogen. Finally, as the abiotic production of hydrocarbons is highly probable to occur at the Lost City hydrothermal field (Proskurowski et al., 2008) and as we do observe organic molecules in the fluids, the fH_2 must be buffered by another hypothetical assemblage (HYP) which could enable such high H_2 concentrations (Fig. 11) and thus expand the organic synthesis domain.

5.4. Natural vs. experimental

5.4.1. Straight chain hydrocarbons

Numerous laboratory experiments of aqueous FTT synthesis under hydrothermal conditions (Horita and Berndt, 1999; McCollom and Simoneit, 1999; McCollom and Seewald, 2001; Rushdi and Simoneit, 2001; McCollom and Seewald, 2003a,b) have described the formation of straight chain hydrocarbons. They are obtained by reduction of CO_2 on the basis of the original gas phase mechanism, which is basically a surface-mineral-catalysed reaction converting gaseous CO to liquid hydrocarbons. However, the hydrocarbon distribution in the hydrothermal fluids is different from the regular one generated by FTT reactions, from which we deduce that other processes are likely taking place besides FTT reactions, such as cracking, surface reactions selectivity or adsorption on rock surfaces. Moreover, some of the compounds could have a biogenic origin which would generate other distribution patterns.

5.4.2. Aromatics

McCollom et al. (2001) have demonstrated the stability of aromatic rings under hydrothermal conditions. In their study, benzoic acid was considered to be in equilibrium with toluene, benzene, phenol and possibly benzaldehyde as a short-lived intermediate. The authors came to the conclusion that, even though, thermodynamically, the degradation of the aromatic ring should occur, kinetic barriers would slow down the reaction and allow the persistence of the aromatic ring in hydrothermal fluids. Furthermore, they suggest that, within the fluids, thermal degradation of alkylated aromatics would lead to the formation of PAHs due to the stability of the ring. Alkylated aromatics have indeed been detected in the fluids and are more than likely supplied by the surrounding organic matter, as they are ubiquitous constituents of living organisms. Consistent with their possible biogenic origin is the presence of toluene, phenol and PAH in the hydrothermal fluids from both Rainbow and Lost City.

5.4.3. Organic acids

Experimental works on lipid formation by aqueous FTT synthesis (McCollom et al., 1999; Rushdi and Simoneit, 2001) resulted in the synthesis of n-alkanoic acids under hydrothermal conditions. This gives support to the presence of these compounds in our samples and their putative formation via the FTT pathway from CO, CO_2 and H_2.

Furthermore, at 300–350 °C and 300 bars n-alkanes undergo oxidation and hydration leading to the production of carboxylic acids (Seewald, 2001), which, in turn, can generate the corresponding (*n*−1)-alkane via deformylation (McCollom and Seewald, 2003b). These results suggest that n-carboxylic acid, n-alkane and (*n*−1)-alkane are related to each other by chemical equilibrium under hydrothermal conditions. Therefore the presence of carboxylic acids together with n-alkanes in our samples is not surprising.

5.5. Carbon isotopic composition

It has been generally stated that thermogenic, biogenic and abiogenic hydrocarbons differ in their carbon isotopic composition. Typical reference values for hydrocarbon gases are (Schoell, 1988; Simoneit et al., 1988): −70 to −60‰ for a biological production, −60 to −40‰ for a thermogenic origin, −30 to −20‰ for geothermal hydrocarbons and −20 to −5‰ for Mid-Ocean Ridges hydrocarbons, but this division is currently highly debated (e.g. Sherwood Lollar and McCollom, 2006; Ueno et al., 2006a,b). However, predicting $\delta^{13}C$ signatures in hydrothermal systems is likely to be complex, due to differences in source $\delta^{13}C$ signatures (i.e., of the C building blocks), and a variety of, mostly unknown, fractionation steps which may occur along the synthesis pathways.

It has been suggested that a decrease of $\delta^{13}C$ with increasing carbon number for gaseous n-alkanes (C_1–C_4) could be an indication of an abiotic formation, while a thermogenic origin has always shown a strongly positive trend (Sherwood Lollar et al., 2002; Pan et al., 2006). In the first case, hydrocarbon formation is likely to occur via catalytic polymerisation of methane and the faster reactivity of $^{12}CH_4$ vs. $^{13}CH_4$ would explain the decreasing trend. Thermogenic processes, on the other hand, occur via cracking and the differences in energy of ^{12}C–^{13}C and ^{12}C–^{12}C bonds leads to more ^{12}C–^{12}C cleavage and thus to depleted light hydrocarbons. Hydrocarbon gases from the Lost City hydrothermal field show a slightly reverse trend and have been suggested to be abiotically produced via catalytic reactions (Proskurowski et al., 2008). Consistently, similar data have been obtained for the alkaline Lost City hydrothermal field (Fig. 12 and Table 5) for methane, ethane, propane and butane (Charlou et al., submitted for publication). The flat profile observed for the acidic Rainbow hydrothermal field (Fig. 12 and Table 5) could account for a major part of abiogenic hydrocarbons with an addition of a minor thermogenic contribution. These catalytic processes are likely to generate heavier hydrocarbons that would infer the abiogenic origin of portion of the C9–C14 n-alkanes present in our samples. Indeed, these longer chain hydrocarbons are likely to be derived from various processes and sources, which, in addition, probably do not lead to a consistent pattern of $\delta^{13}C$ vs. carbon number. As a result, interpreting the $\delta^{13}C$ trend with carbon number would be totally speculative for heavier hydrocarbons. Moreover, even for gaseous hydrocarbons, abiotic synthesis under experimental hydrothermal conditions does not always lead to a reversal trend for C_1 to C_4 (Fu et al., 2007), which is likely to depend on the reaction pathway. Again, multiple carbon sources and unknown reaction pathways that occur in hydrothermal systems do not allow a conclusion to be drawn at present.

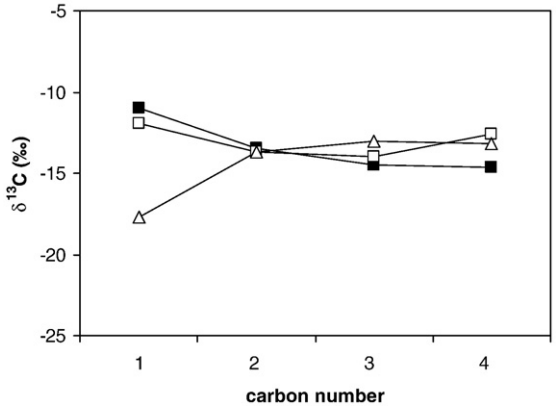

Fig. 12. Plot of δ13C values of n-alkanes against carbon number. No isomeric distinction was done for butane. Squares refer to the Lost City data; full for Proskurowski et al. (2008) and empty for this study (EXOMAR cruise 2005). Triangles refer to the Rainbow data.

Table 5
Carbon isotopes data from the Lost City and the Rainbow hydrothermal vent fields

Site	Location	*T* (°C)	$\delta^{13}C$ (PDB) ‰			
			CH_4	C_2H_6	C_3H_8	C_4H_{10}
Lost City[a]	Beeheve	90	−11.0	−13.5	−14.5	−14.6
Lost City[b]	Beeheve	93	−11.9	−13.7	−14.0	−12.6
Rainbow[b]	EXO-D7-Ti1	343	−17.7	−13.7	−13.0	−13.2

[a] Proskurowski et al. (2008).
[b] This study (EXOMAR cruise 2005).

Individual $\delta^{13}C$ data for hydrocarbons detected in our samples ranged from −46 to −20‰ (Table 4), which is consistent with the $\delta^{13}C$ of the n-alkanes found in Lost City's serpentinites (−38.6 to −24.6‰) (Delacour et al., 2008). In general, −26‰ is the average value given for the bulk sedimentary organic carbon (Schidlowski, 1987), implying a possible biogenic origin of the compounds having such an isotopic ratio. In addition, $\delta^{13}C$ values around −46‰ are agreed to be a typical biogenic signature for hydrocarbons. However, in a recent FTT synthesis laboratory experiment by McCollom and Seewald (2006), abiogenic n-alkanes showed stable isotope signatures similar to those of the source CH_4 (~ −50‰) and ~35‰ depleted vs. source CO_2 over the entire range of C numbers studied (C_{12}–C_{27}). In our study, hydrocarbons in the fluids did not have a constant $\delta^{13}C$ value over the range of C number (C_9–C_{14}) but, on average, they exhibited a depletion of 35‰ and 26.2‰ in comparison to CO_2 at Rainbow and Lost City, respectively ($\delta^{13}C_{(CO2\text{-}Rainbow)}$=+1 to −3‰ (Lein et al., 2000; Charlou et al., 2002) and $\delta^{13}C_{(CO2\text{-}LostCity)}$ estimated to −9‰ (Proskurowski et al., 2008)). Finally, it appears elsewhere (McCollom and Seewald, 2007) that first of all too few of such experiments that have been conducted so far; then that the isotopic fractionation patterns are definitely inconsistent between those similar experiments. Hence, the isotopic signature of organic molecules generated by FTT synthesis seems unpredictable and the $\delta^{13}C$ value of one compound may not be the key in determining its origin.

As mentioned earlier, n-alkanoic acids were found to be enriched in ^{13}C vs. n-alkanes of the same chain length (Table 4 and Fig. 10), a trend that was similarly observed in oil field waters (Franks et al., 2001). This would run counter to the generation of alkanoic acids from alkanes via carbon oxidation, for which ^{12}C is more reactive (Pan et al., 2006). In addition, this would also be inconsistent with the abiotic synthesis of lipids from formic acid by FTT synthesis via a succession of addition–reduction of CO units (Rushdi and Simoneit, 2001). On the contrary, isotopically enriched carboxyl carbons relative to aliphatic carbons have been actually suggested to be indicative of biological processes (Abelson and Hoering, 1961; Rinaldi, 1974). Organic acids found in the hydrothermal fluids might then be biogenic.

5.6. Relevant compounds for the origin of life

It has been proposed that the origin of life required self-assembly of molecular systems (Koch, 1985; Deamer, 1997; Segré et al., 2001). Therefore surfactants have been suggested to be present at the origin of the first cell membranes (Ourisson and Nakatani, 1994; Deamer et al., 2002; Walde, 2006) and these membranes could be viable for further evolution of life (Trevors, 2003). Such amphiphilic molecules (i.e., composed of a hydrophobic tail and a hydrophilic head) have the ability to assemble spontaneously via hydrophobic interactions.

Depending on their concentration, they especially form organised structures from a chain length of 6 carbon atoms and bi-layers from 8 carbon atoms. Long chain carboxylic acids (from C_9) have these properties and indicate that membranes can probably form in hydrothermal environments. Even though the stability of such membranes at high pressure and temperature is debated, PAH can contribute stabilising them as cholesterol does in cell membranes of living organisms today (Deamer et al., 2002). In addition, lipid products detected in the fluids are of interest due to their potential for generation of secondary products such as esters and peptide oligomers (Tsukahara et al., 2002) and decanoic acid draws particular attention because it resembles acids that drive metabolic reactions (Hazen et al., 2002).

Other key molecules for life to happen and propagate (Ferris, 1992; Ferris et al., 2004; Ferris, 2005), such as purines, pyrimidines, N-bearing heterocyclic compounds, amino-acids, phosphorus compounds, have not been detected using the analytical approaches in this study. However, they would be worth investigation.

6. Conclusions

A clear enrichment of semi-volatile organic compounds (C6–C18) of fluids from the Rainbow and the Lost City ultramafic-hosted hydrothermal systems was revealed in this study. Despite greatly differing pH, temperature and inorganic chemistry, the fluids from both vents have a high reducing power due to high H_2 content and they showed the presence of similar compounds. One major difference, however, was the clear enrichment in aromatic compounds of the Lost City fluids.

N-alkanes, which were detected at both locations, are known to persist in various geological environments even at high temperature and are typical products of FTT synthesis. Their formation from CO_2 is thermodynamically favourable under the conditions encountered at both sites. In addition, they have been detected in many experimental studies on aqueous FTT synthesis. This suggests that at least part of the n-alkanes detected in hydrothermal fluids were produced by FTT reactions. Redox reactions are thought to occur between n-alkanes and n-alkanoic acids. Therefore this portion the n-alkanoic acids would also be abiogenic. Compound-specific stable isotope data were obtained for both n-alkanes and n-alkanoic acids. However, this data was insufficiently diagnostic to uniquely support a biogenic, or an abiogenic origin. Branched alkanes as well as aromatic compounds are likely to be derived from degradation of surrounding organic matter, which could either have been brought in by seawater via the recharge zones, or supplied by deep subsurface bacteria flushed by hydrothermal circulation. Branched alkanes are indeed found in sediments (Greenwood et al., 2004) and methyl alkanes are common in cell membranes (Jahnke et al., 2004). The presence of cycloalkanes could not be explained at this stage.

Several processes, both biogenic and abiogenic, leading to the formation of organic compounds are likely to occur simultaneously in hydrothermal systems. As a result, unusual distributions of compounds and complex isotope fractionations are expected. Therefore, further investigation is needed to clarify the origin of the organic molecules detected in the Rainbow and Lost City fluids. However, with the data at hand, we suggest that a mixed origin of the compounds is probable.

Finally, all the processes that could occur in hydrothermal systems are still not well understood yet. Nor is it known where the particular reactions called upon herein are most likely to take place. For instance, the behaviour of seawater in supercritical state and the chemistry driven by such conditions is not well constrained. Supercritical seawater would be a favourable medium for C–H bond formation and thus a favourable place to synthesise organic molecules could be in the neighbourhood of the magmatic reservoir (T>400 °C).

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