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Origin of organic compounds in fluids from ultramafic-hosted hydrothermal vents of the Mid-Atlantic Ridge

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Abstract

Natural gas, primarily methane (CH_4), is produced in substantial amounts in ultramafic-hosted hydrothermal systems. These systems could also generate oil (heavier hydrocarbons) and the first building blocks of life (prebiotic molecules). In the presence of iron bearing minerals, serpentinisation reactions generate H_2. Subsequently, CH_4 could be synthesised by Fischer-Tropsch Type (FTT) reaction ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$) which is an abiotic process. This has lead to the idea of abiotic formation of larger organic molecules. Both thermodynamics and laboratory work support this idea, yet field data have been lacking. This study focuses on determining the organic content of fluids from ultramafic-hosted hydrothermal systems from the Mid-Atlantic Ridge (MAR) and the origin of the compounds. Fluids were collected from the Lost City, Rainbow, Ashadze and Logatchev vent fields during the EXOMAR (2005), SERPENTINE (2007), MoMARDREAMnaut (2007) and MOMAR08-Leg2 (2008) cruises conducted by IFREMER, France. A SBSE-TD-GC-MS technique was developed and used to extract, concentrate, separate and identify compounds in the fluids. Hydrothermally derived compounds appeared to consist mainly of hydrocarbons and O-bearing molecules. In addition, some amino acids were detected in the fluids by ULPC-ESI-QToF-MS but their origin will need to be determined. The organic content of the Rainbow fluids did not show intra field variability unlike differences that could be noted over the years. In order to address the question of the source of the molecules, compound specific carbon isotopic analyses were carried out and completed with a bacterial (*Pyrococcus abyssi*) hydrothermal degradation experiment. The $\delta^{13}C$ data fall in the range of -40 to -30‰ (vs. V-PDB), but individual $\delta^{13}C$ values preclude the identification of a biogenic or abiogenic origin of the compounds. The degradation experiment, however, suggests an abiogenic origin of a portion of saturated hydrocarbons whereas carboxylic acids would be biogenic, and aromatic compounds would be thermogenic.

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Front cover: © Ifremer/ Exomar 2005, Victor 6000 dive #268/ carbonate chimney, Lost City, MAR 30°N. (left)
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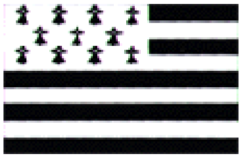
A ma grand-mère de Lesneven, (Pa)^2 et maman, Vincent, Nicolas, mes amis.



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Paper I: Konn, C., Charlou, J.L., Donval, J.P., Holm, N.G., Dehairs, F. and Bouillon, S., 2009. Hydrocarbons and oxidized organic compounds in hydrothermal fluids from Rainbow and Lost City ultramafic-hosted vents. *Chemical Geology*, **258**(3-4): 299-314.

Paper II: Konn, C., Charlou, J., Donval, J. and Holm, N.G., Detection of trace organic compounds by Stir Bar Sorptive Extraction: application to the evolution of the organic composition of hydrothermal fluids from the Rainbow site (36N, Mid-Atlantic ridge) over 3 years. *Submitted to Applied Geochemistry.*

Paper III: Konn, C., Testemale, D., Querellou, J., Holm, N.G. and Charlou, J.L., New insight on the origin of organic compounds in fluids from ultramafic-hosted hydrothermal systems. *Submitted to Geobiology*.

Paper IV: Konn, C., Magnér, J., Charlou, J.L., Holm, N.G. and Alsberg, T., Detection of trace concentrations of amino acid in aqueous solutions by Ion-pairing reversed-phase UPLC-ESI-QToF-MS: application to hydrothermal fluids. *Submitted to Geochemical Transactions.*

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All work in this thesis has been carried out by the author except cell culture (Paper III) and EXOMAR cruise (2005) sample collection and preparation (Paper I). The high P&T experiments were carried out by Denis Testemale, however I was present and may be able to carry them out myself in the future. I participated in 3 cruises conducted by Ifremer for sample collection and preparation: SERPENTINE (2007), MoMARDREAMnaut (2007) and MOMAR08-Leg2 (2008). I carried out all GC-MS and GC-IRMS sample analyses. UPLC-QToF-MS method development and analyses were carried out both by me and Jörgen Magnèr. I was lead author on all papers and did data interpretation as well as the writing.

Stockholm, July 2009-07-14
Cécile Konn

1 Introduction

Hydrothermal circulation is a phenomenon taking place over the entire planet and refers to the circulation of fluids within the hot Earth’s crust and mantle. External manifestations of hydrothermal activity are both observed on land (geysers and hot springs) and at the seafloor (black smokers). On the hypothesis that life began on Earth, without any import of extraterrestrial material, submarine hydrothermal systems have been postulated to be very favourable environments for the origin of life. Physico-chemical conditions encountered at deep sea hydrothermal vents may indeed be well representative of presumed conditions on the early Earth at the earliest Archean (~3.8 Ga ago), when life is assumed to have emerged. The key in the emergence of life is primary carbon fixation, which is the fact of extracting carbon from a mineral source (air, rocks, water...) and converting it to organic carbon, i.e. incorporated into organic molecules built on carbon, oxygen, hydrogen and nitrogen. All living organisms feed on carbon and process it to produce its biomass (tissues, cells...). Hydrothermal systems may produce methane (CH_4) from carbon dioxide (CO_2) and hydrogen (H_2) via pure chemical reactions, which represent a form of carbon fixation via an abiotic process. Hence one may ask: would hydrothermal systems have been able to generate other organic compounds that would have provided the first material for life to start? Moreover, to a totally different aspect, this so-called abiogenic methane, which is produced together with other light hydrocarbon gases (ethane, propane, butane), raises the question of the formation of abiogenic oil which opposes the generally agreed theory that oil only comes from the thermal decomposition of ancient compacted fragments of plants and animals. Is the quantity of abiogenic natural gas (i.e. CH_4) generated by hydrothermal systems significant? Could heavier oil be also produced in such environments? One can assess the great importance of such a hypothesis for the industry of oil. In a global approach the question that rises is: “Are abiogenic organic molecules produced in submarine hydrothermal systems?”

A lot of data on thermodynamic calculation and experimental work is available and strongly support the feasibility of abiotic synthesis of a wide range of organic compounds under hydrothermal conditions. Nevertheless, field data was obviously lacking and is urgently needed.

Introduction (français)

La circulation hydrothermale est un phénomène répandu à l'échelle de la planète qui désigne la circulation de fluides dans la coûte et le manteau terrestre. Les manifestations extérieures de l'activité hydrothermale sont à la fois terrestres (geyser et sources chaudes) et océaniques (fumeurs noirs). Les systèmes hydrothermaux sous-marins constitueraient des environnements vivement favorables pour l'origine de la vie sur Terre, dans l'hypothèse où cette dernière aurait été initiée sans aucun apport de matière extraterrestre. Les conditions physico-chimiques rencontrées dans les systèmes hydrothermaux des grands fonds seraient, en effet, représentatives des supposées conditions qui régnaient sur la Terre primitive lorsque la vie serait apparue au tout début de l'Archean (il y a ~3.8 Ga). La fixation primaire du carbone est indispensable à l'émergence de la vie et en constitue la clé de voûte. Ce processus se défini par l'extraction du carbone d'une source minérale (eau, air, roches) et la conversion de ce carbone inorganique en carbone organique c'est à dire l'incorporation dans des molécules organiques qui sont formées de carbone, oxygène, hydrogène et azote. A noter que tout organisme vivant se nourrit de carbone afin de construire sa biomasse (tissus, cellules...). Les systèmes hydrothermaux produiraient du méthane (CH_4) à partir de dioxyde de carbone (CO_2) et d'hydrogène (H_2) uniquement via des procédés chimiques, ce qui constitue une forme de fixation primaire du carbone par un procédé dit abiotique car aucun organisme vivant donc qu'aucun processus biologique n'intervient dans la fabrication. Ainsi peut-on évoquer la question suivante: les systèmes hydrothermaux ont-ils été capables de produire d'autres composés organiques qui auraient constitué la matière première nécessaire à la naissance de la vie? Par ailleurs, dans un tout autre registre, la formation du méthane abiogénique, qui s'accompagne de la synthèse d'autres gaz hydrocarbures légers (éthane, propane et butane), soulève la question de la production abiotique de pétrole ce qui s'oppose à la théorie communément acceptée affirmant que le pétrole provient de la décomposition thermique d'ancien fragments de plantes et animaux sédimentés puis compactés. Mais la quantité de gaz naturel (principalement CH_4) abiogénique générée par les systèmes hydrothermaux est-elle conséquente? Est-ce que des huiles plus lourdes (i.e. précurseurs des carburants) pourraient également être produites dans ces mêmes environnements? L'on voit ainsi toute l'importance d'une telle hypothèse pour l'industrie pétrolière. Dans un contexte global, la question qui se pose est : «Les systèmes hydrothermaux océaniques produisent-ils des composés organiques de façon abiogénique ?».

To fill the gap and to address the question of abiogenic organic synthesis, we collected hydrothermal fluids from different hydrothermal vents of the Mid-Atlantic Ridge and analysed for organics. At first a method to extract, concentrate and characterise organic molecules in hydrothermal fluids was established and is described in papers I and II. Then the focus was kept on identifying and listing all potential hydrothermally derived compounds in different geological settings and constitutes the main purpose of paper I. However, two questions remained: where in the system are these compounds produced? And are they abiogenic or biogenic (i.e. biologically derived)? In Paper II we investigated the intra-field variability in an attempt to discriminate between local production (within the black smoker) and global production deeper in the mantle. In order to address the second question, Paper III presents a new approach complementary to the traditional carbon isotopic ratios which used alone is inconclusive. Eventually specific compounds more relevant to the origin of life, namely amino acids, were investigated in the fluids which was the aim of Paper IV. The main conclusions that follow are that a portion of the saturated hydrocarbons may be abiogenic, whereas fatty acids would be biogenic and aromatic compounds would be thermogenic (= process of degradation of a biogenic carbon source at elevated temperature and pressure). The reactions probably occur deep in the mantle at temperatures >400°C. Amino acids are most likely present in hydrothermal fluids however their origin has not been investigated.

2 Mid-Ocean Ridges hydrothermal systems

The first deep sea hydrothermal systems were discovered in the late 1970s in the Pacific Ocean on the Galapagos rift. Since then, numerous hydrothermal fields, mainly located at the ridge axis were discovered along all spreading ridges, including the slow-spreading Mid-Atlantic Ridge (MAR): e.g., the Trans-Atlantic Geotraverse (TAG) (Scott et al., 1974), Lucky Strike (Charlou et al., 2000), Menez Gwen (Charlou et al., 2000), Broken Spur (Murton et al., 1994), Snakepit (Campbell et al., 1988) and MARK hydrothermal systems (Kelley et al., 1993). All these systems are hosted on mafic rocks and derive their energy from an axial magma chamber being the sole heat source of the system.

Il existe énormément de données thermodynamiques et de résultats expérimentaux qui soutiennent fortement la faisabilité de synthétiser une large gamme de composés organiques de manière abiogénique, en conditions hydrothermales. Néanmoins, un manque évident de données de terrains devait être absolument et rapidement comblé. Pour ce faire et pour répondre à la question de la synthèse organique abiotique, nous avons collectés des fluides de différents évents hydrothermaux sur la dorsale Médio-Atlantique et nous les avons analysés afin d'y rechercher des composés organiques. En premier lieu une méthode permettant d'extraire, concentrer et caractériser les molécules organiques a été établie et est décrite dans les papiers I et II. Ensuite l'attention a été portée sur l'identification et le recensement de tous les composés potentiellement issus de l'activité hydrothermale dans différents environnements géologiques et ceci constitue le but principal du papier I. Cependant, deux questions restaient sans réponse: à quel endroit dans le système ces composés sont-ils produits ? Et sont-ils abiogénique ou biogéniques (i.e. dérivés de matière biologique)? Dans le papier II nous avons étudié les variations de composition organique à l'intérieur d'un même site hydrothermal dans le but de discriminer la production locale (échelle du fumeur noir) de la production globale (échelle d'un site hydrothermal). Le papier III visait à répondre à la seconde question et présente une nouvelle approche pour l'identification de l'origine des composés organiques dans les fluides hydrothermaux. Cette approche est complémentaire à la méthode traditionnelle de la mesure des rapports isotopiques de carbone qui utilisée seule ne permettrait pas de conclure. Finalement, des composés plus spécifiques et importants dans la question de l'origine de la vie, dans notre cas les acides aminés, ont été étudiés dans le papier IV. On peut établir au jour d'aujourd'hui des conclusions majeures : (i) une partie des hydrocarbures saturés présents dans les fluides hydrothermaux seraient abiogéniques, alors que les acides gras seraient biogéniques et les composés aromatiques seraient thermogéniques (= processus qui consiste à dégrader une source de carbone biogénique à hautes température et pression) ; (ii) les réactions se déroulent certainement à grande profondeur dans le manteau à des températures supérieures à 400°C ; (iii) il est plus que probable que les acides aminés soient présents dans les fluides hydrothermaux bien que leur origine reste à déterminer.

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The mafic rocks are typically basalts, which are hard and non-porous material. Therefore hydrothermal circulation occurs through a limited number of major cracks that result from the combination of magmatic and tectonic processes at the axis ***(Figure 1)***. Resulting venting is characterised by high temperatures (up to 360°C) and acidic fluids (pH ~ 2-3) that are significantly enriched in magmatic volatiles (e.g. CO_2). The precipitation of these fluids when mixing with seawater leads to the formation of chimney-like, sulfide structures called black smokers because of the black plume they generate, actually due to the presence of black suspended manganese oxide MnO_2 particles (precipitation of the seawater Mn when mixing the hot fluids) as well as ferrous oxide $Fe(OH)_3$ particles (precipitation of the hot fluid Fe when mixing with cold seawater).

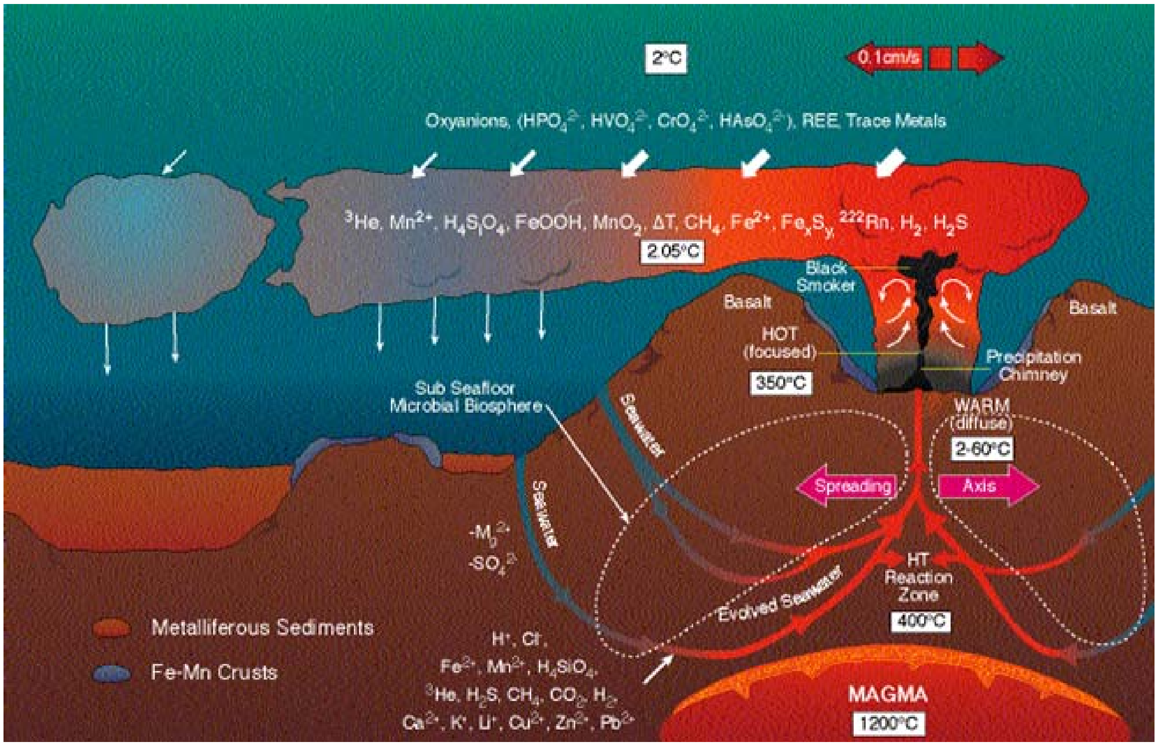


Figure 1: cartoon illustrating the hydrothermal circulation and the evolution of the fluid composition during its journey in the subsurface. (From NOOA website)

Mid-ocean ridge generation is driven by magmatic and tectonic processes, which result from seafloor spreading. In the case of slow spreading ridges (full spreading rate <~5 cm/year), spreading is accommodated by the formation of a conjugated faults network that, in many places in the Atlantic Ocean, lift mantle peridotites up to the ocean floor ***(Figure 2)*** e.g. (Cannat, 1993;

Cannat et al., 1997; Lagabrielle et al., 1998). This phenomenon is referred to as tectonic accretion by opposition to the magmatic accretion in the case of basaltic systems.

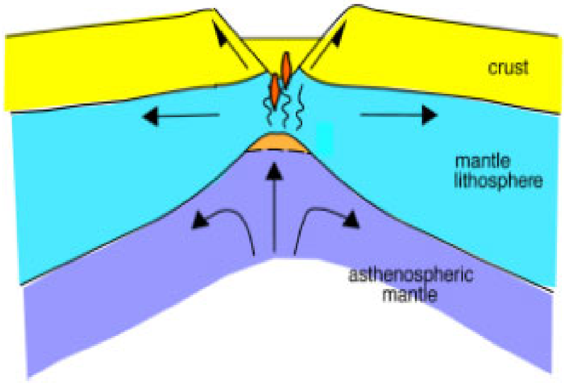


Figure 2: Schematic view of a slow spreading ridge showing the large extensional faults that form the walls of the axial valley and bring up the most superficial levels of the mantle. These superficial levels are called lithospheric mantle because the peridotites are relatively cold (less than 1000 °C) and stiff there. Below, we find asthenospheric mantle where the peridotites are warmer and softer. From © Mathilde Cannat CNRS / IPGP - http://www.ifremer.fr/serpentine/english/scientific-sheet-5.htm)

The first hydrothermal system located on such an outcrop was identified in 1993 along the slow-spreading MAR. The Logatchev hydrothermal field was the first ultramafic-hosted vent area to be discovered of a series of five known today: Logatchev (Batuev et al., 1994), Rainbow, Ashadze (Serpentine-Cruise-Ifremer, 2007), Lost City (Kelley et al., 2001) and Nibelungen (Melchert et al., 2008) (***Figure 3***). The composition of the crust lying underneath those systems appears to be highly heterogeneous, unlike the basalt crust hosting mafic systems, and a well-constrained model has not yet been established. However, the known geology around these sites support the idea that this type of crust is schematically best pictured with the plum-pudding model that describes the crust as discrete gabbro bodies in a serpentinised peridotite matrix (primarily olivine and pyroxene minerals), locally capped by a thin layer of basalt (Cannat et al., 1997; Ildefonse et al., 2007), and which is speculated to represent a significant portion of the lithosphere formed at slow-spreading ridges.

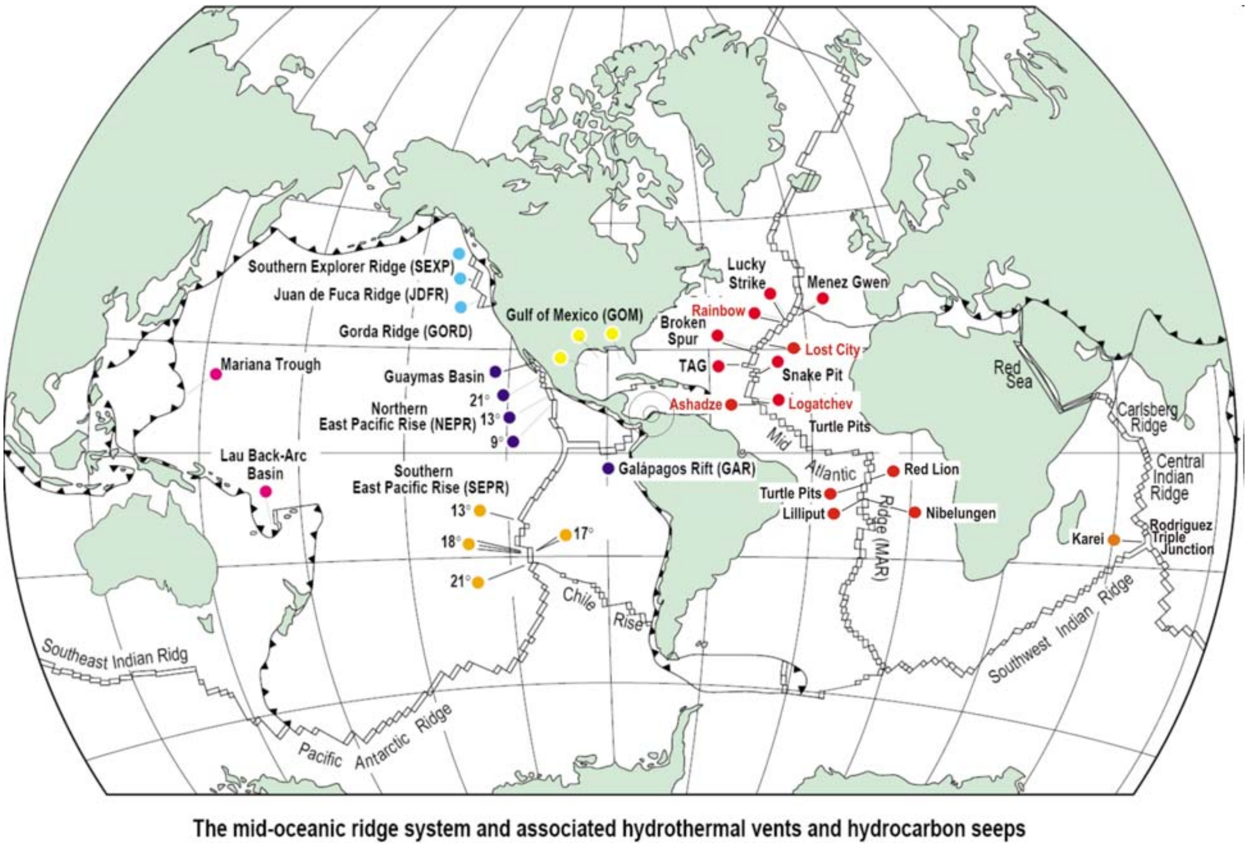


Figure 3: Modified after Van Dover et al. (2002). Map of known hydrothermal vents and major mid-ocean ridges. Written in red are the names of the hydrothermal fields studied in this work.

The faults allow seawater to penetrate this crust; then hydrothermal circulation takes place through the faults network. Seawater / rock interactions result in the alteration of the minerals; in the case of peridotites the alteration processes can be described by several chemical equilibria that are lumped together under the general term of serpentinisation and that globally generate heat and high amounts of H_2 (O'Hanley, 1996; Frost and Beard, 2007). The serpentinisation reactions prevailing under those systems conditions generate fluids sharing similar characteristics with fluids from basalt-hosted systems, i.e. high temperature (250 - 350°C), low pH (~ 2-3), and enrichment in CO_2 (10-16 mM), but also carrying their own peculiarities such as high concentrations of H_2 (10-26 mM) and CH_4 (1-3 mM) (Charlou et al., 2002; Douville et al., 2002; Melchert et al., 2008). Precipitation of the fluid with cold seawater generates the formation of anhydrite ($CaSO_4$) chimney (black smokers, ***Figure 4***) together with extensive massive sulfide deposits.

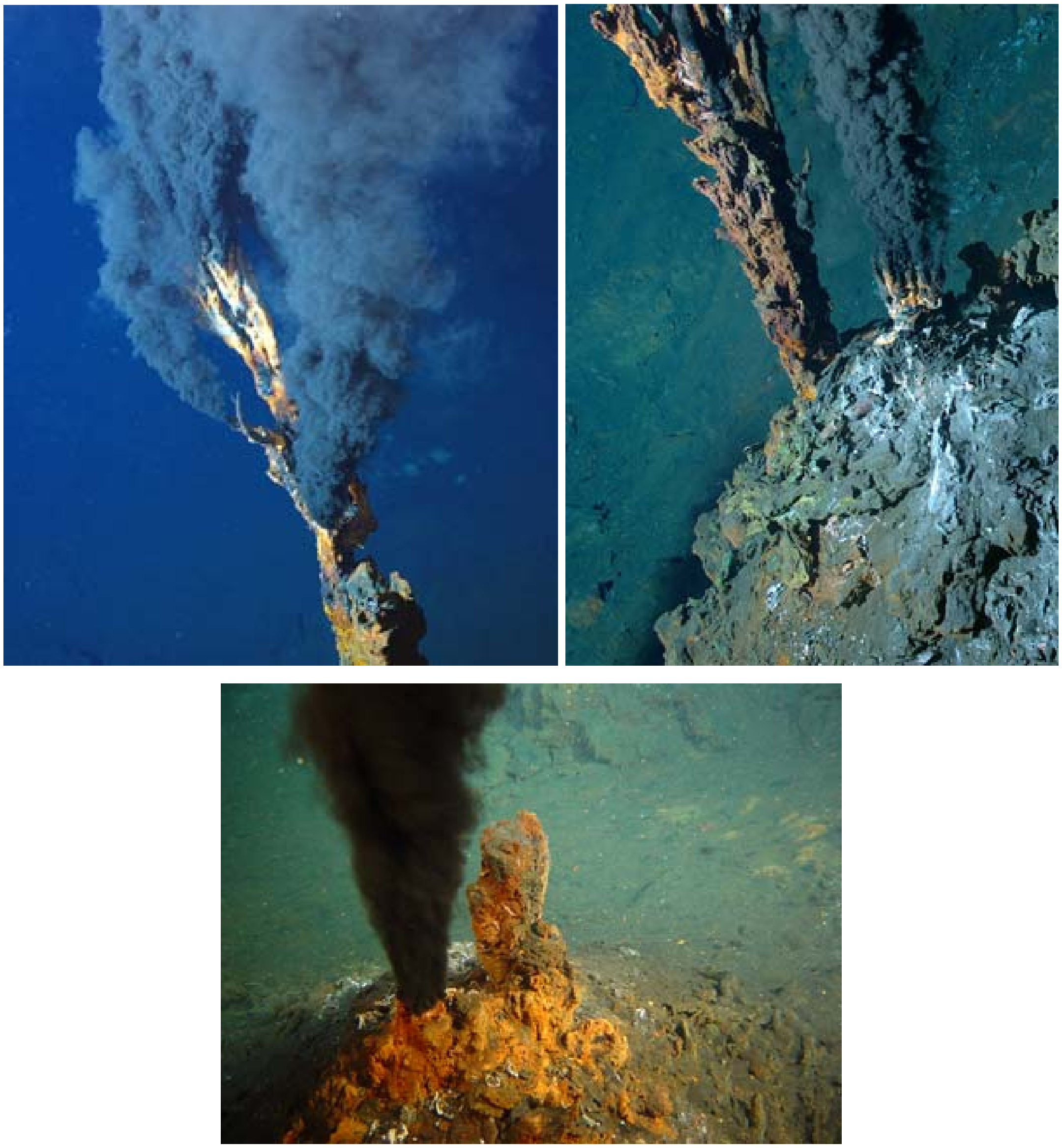


Figure 4: Black smockers at the Rainbow hydrothermal field. Images © Ifremer / MoMARDREAMnaut 2007 and MOMAR08-Leg2 2008 cruises.

Even though the heat source driving ultramafic-hosted hydrothermal systems is still debated, the sole serpentinisation reaction is not believed to generate high enough heat flow and temperatures, and an additional heat input related to magmatic activity is most likely needed (e.g. Allen and Seyfried, 2004; Petersen et al., 2009). In particular, the role of gabbros as a heat source has been described for the Rainbow and the Lost City fields (McCaig et al., 2007; Ildefonse et al., 2008). Petersen et al. (2009) also reported the indication of extrusive volcanic activity by pillow basalt outcrops without any sedimentary cover in the rift valley just west of the Logatchev fields. The authors also suggest that the heat of mafic intrusions, which are observed in the footwall, could be mined by faults rooting at or close to the ridge axis.

The Lost City Hydrothermal Field is so far one of its kind and was discovered in 1997 15km off the MAR ridge axis at 30°N. Also hosted on peridotites rich outcrops, typical ultramafic-hosted vent concentrations of H_2 and CH_4 are observed. The only serpentinisation equilibria dominating here result in low-temperature (<90°C) and alkaline (pH=10-11) fluids as well as low CO_2 concentration (<<1 mM) (Kelley et al., 2001; 2005). Moreover, these fluids are rich in calcium and mixing with seawater leads to the formation of large carbonate chimneys.

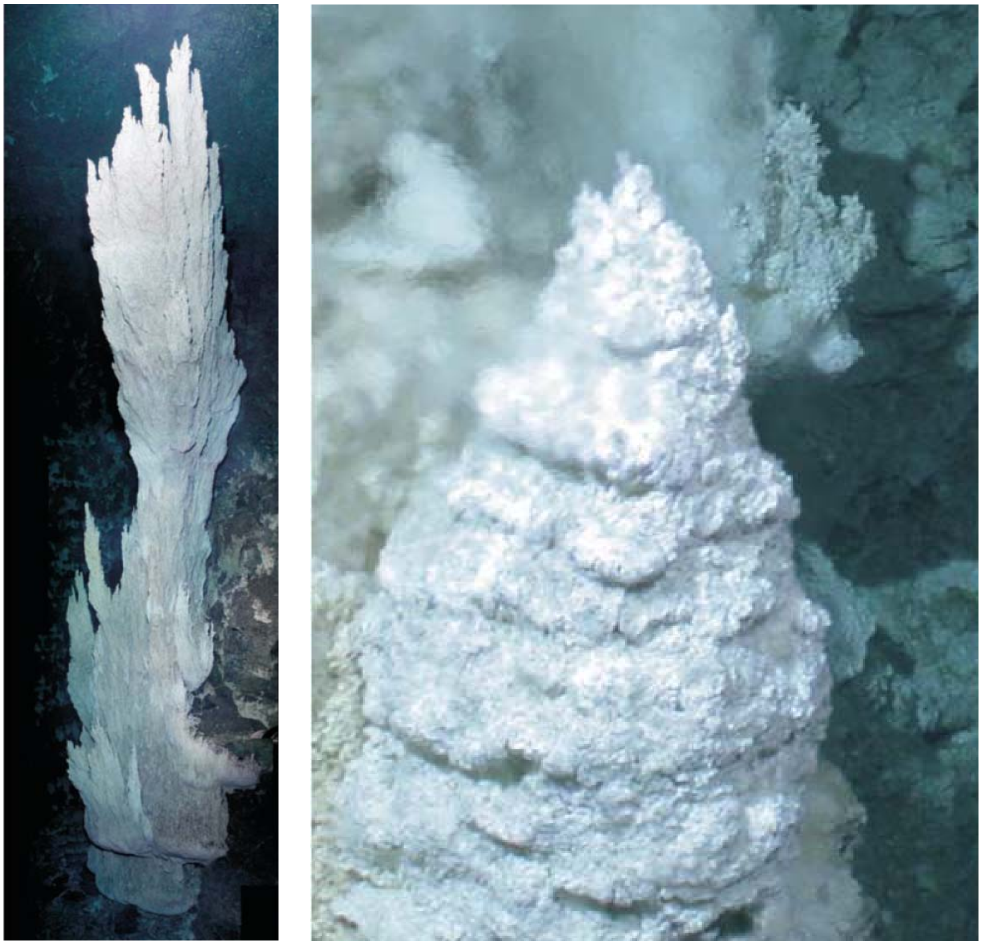


Figure 5: Carbonate chimneys at the Lost City hydrothermal field. Images from Ludwig et al. 2006 (right) and Kelley et al. 2005 (left).

3 Geological settings and main features of the study areas

Table 1: Main features about the studied hydrothermal vents and end-members value for Cl^-, CO_2, CH_4, H_2, H_2S in their fluid. [1](Charlou et al., 2002), [2](Kelley et al., 2005), [3] EXOMAR cruise (2005), [4](Schmidt et al., 2007), [5] SERPENTINE cruise (2007) and [6](Charlou et al., InPress).

	Location	*pH*	*T (°C)*	*Depth (m)*	*Cl^-*	*CO_2*	*CH_4*	*H_2*	*H_2S*
Rainbow	36°13'N	3 - 4[1]	350[1]	2300[1]	780[1]	16[1]	2.5[1]	16[1]	1.2[1]
Lost City	30°07'N	10 - 12[2,3]	90[3]	750[3]	548[3]	<<1[2,*]	1-2[2,*]	<15[2,*]	0.1-0.3[3]
Ashadze1	12°58'N	3 - 4[5]	350[5]	4100[5]	614[6]	3.7[6]	0.5[6]	8-19[6]	0.8-0.9[5]
Ashadze2	12°58'N	-	-	3260[5]	326[6]	-	0.8[6]	26[6]	<0.1[5]
Logatchev1	14°45'N	3 - 5[1,4,5]	350[5]	3000[5]	512[6]	3.6[6]-10.1[1]	2.1[1]-3.5[4]	9[6]-19[4]	0.8-2.5[1,4,5]
Logatchev2	14°43'N	4 - 5[5]	350[5]	2700[5]	126[6]	6.2[6]	1.2[6]	11[6]	1.8[5]

*** not end member values**

N.B.: Fluids are characterized by their end member values, i.e. extrapolated values at magnesium concentration normalized to zero. In ultramafic-hosted systems, Mg is efficiently removed from hot seawater and precipitated during rock alteration and thus pure hydrothermal fluids are considered to be Mg-free (Mottl and Holland, 1978).

3.1 Rainbow

The Rainbow hydrothermal field is located on the Mid-Atlantic Ridge (MAR), south of the Azores at 36°14'N, 33°54'W at a 2300 m depth (***Figure 3, Table 1***) (German et al., 1996; Bougault et al., 1998; Charlou et al., 2002). It stands on the west-facing flank of the Rainbow ridge at the northeastern corner at the intersection between the Azores Mid-Atlantic Ridge (AMAR) segment and the south AMAR segment being also the intersection of the non-transform fault system and the ridge faults. The field is about 250 m (east-west) by 60 m (north-south) in size and consists of at least 10 groups of highly active black smokers, which are located on an ultramafic block and distributed over the entire field (***Figure 6***). The most abundant recovered rock type in that area is peridotite (harzburgite and dunite) that presents a variety of serpentinization styles and intensity, and a variety of deformation styles. Serpentinites are frequently oxidized. Some peridotite samples have melt impregnation textures. Variously evolved gabbroic rocks also occur as discrete samples or as thick dikes in peridotites. The southwestern and northeastern flanks of the massif appear to consist of basalts and fresh basaltic glass. The western border of the field is a 25 m high fault scarp where stockwork mineralisation is observed and is made of massive sulfides, strongly altered serpentinites, and breccias containing elements of iron sulfide/oxide impregnated serpentinites (Ildefonse et al., 2008). The uniformity of end-member major-, minor, trace-elements concentrations and gas contents suggests that all Rainbow fluids originate from the same deep source (Charlou et al., 2002).

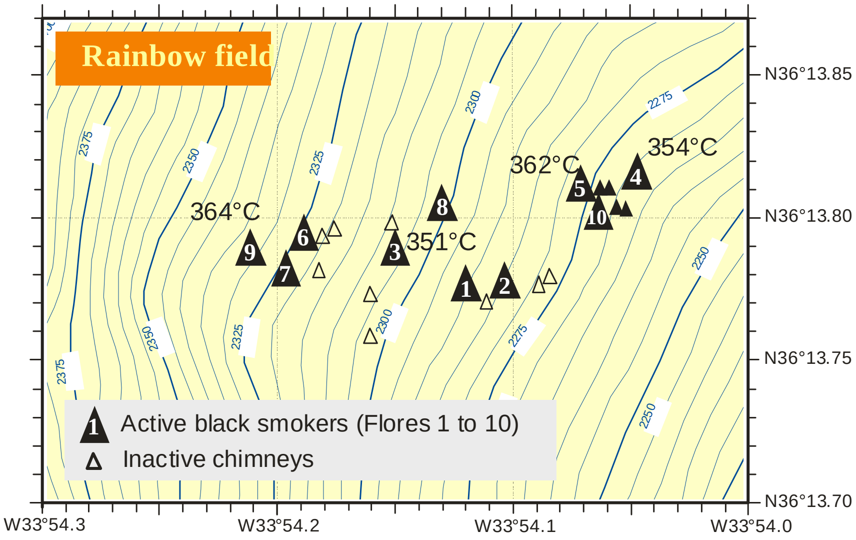


Figure 6: Location of active black smokers at the Rainbow hydrothermal field (From Charlou et al., 2002). This map was established during the FLORES 1997 cruise but the smokers were resampled during the EXOMAR 2005, MoMARDREAMnaut 2007 and MOMAR08 - Leg 2 2008 cruises all conducted by Ifremer. Full triangles correspond to active black smokers whereas empty triangles represent inactive chimneys.

3.2 Lost City

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 ***(Figure 3, Table 1)***. The massif rises to 700 m below the sea surface, is terminated in the south by the Atlantis transform fault, and is bounded to the East by a nodal basin that is down to 6000 m deep ***(Figure 7)***. The field, which extends over 400 m in length, is composed of active, inactive, and fissure-filling carbonate formations. The top of the scarps to the northwest and northeast of the field comprises of variably foliated serpentinite, talc-amphibiole schist and metagabbroic rocks. A shear zone occurs near the summit of the massif, which is capped by 1 to 3m of flat-lying sedimentary breccias overlain by fossiliferous pelagic limestone. The basement rocks in the vicinity of the field are cut by veins of calcite and aragonite, which derive from some of the oldest hydrothermal activity at this site (Kelley et al., 2005). Früh-Green et al. (2003) have shown that hydrothermal activity has been active for at least 30,000 years in this zone.

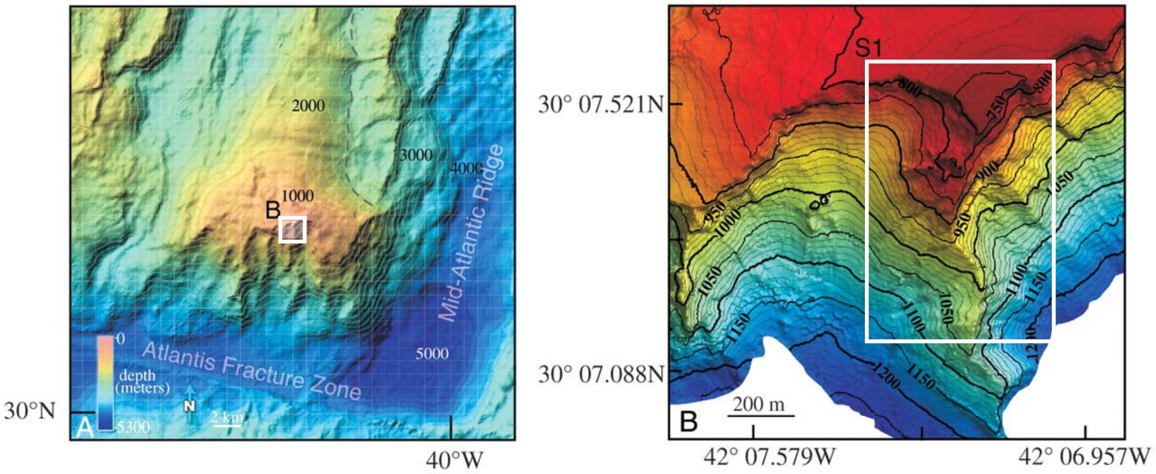


Figure 7: A. Location map of the Atlantis Massif at 30°N along the Mid-Atlantic Ridge (MAR). The white box indicates the location of the Lost City Hydrothermal Field on the southern ridge of the massif. B. Southern wall of the Atlantis Massif. The white box shows the areal extent of the Lost City vent field, located on a terrace of the southern wall. (From Kelley, D. S. et al., 2005)

3.3 The 14°45’N area

The MAR between the Fifteen-Twenty and Marathon Fracture Zone is characterized by three short ridge segments (13°N, 14°N and 15°N segments) interrupted by non-transform discontinuities (Cannat et al., 1997). Recently the SERPENTINE cruise revisited this region and based on seafloor morphology, dive observations, and rock sampling, Cannat and coworkers developed a model whereby ultramafic-hosted hydrothermal venting in the 13-15°N region involves both large active normal faults, and an inside corner-type position relative to a small offset of the volcanic axis (Cannat et al., 2007). Asymmetric accretion and oceanic core complex formation prevails in the 15°N (Logatchev) and 13°N (Ashadze) areas (Escartin et al., 2008).

3.3.1 Ashadze

The Ashadze hydrothermal field was discovered at 12°58’N, 44°50W in 2003 by Russian scientists (Beltenev et al., 2003; 2005) ***(Figure 8)*,** further described in 2005 and explored in 2007 during the SERPENTINE cruise conducted by Ifremer. It comprises 2 active sites (Ashadze 1 and Ashadze 2) 5 km apart ***(Figure 9)*** located at a distance of 4 and 9 km, respectively, off the rift axis. Active vents at Azhadze 1 (4100 m) are distributed over an area about 150 m-long, along an EW-trending south-facing scarp. High resolution mapping at 20 m (450x450 m area) reveals the fine structure of sulfide mounds, as well as complex fissure arrays near the vents (Ondreas et al., 2007). Ashadze 2 is composed of three subfields of 200 x 100 m at a depth of 3260 m. Black smokers are located in a crater-shaped depression, about 25 m in diameter, which lies in a narrow (about 70 m), N-S trending trough. On the high resolution maps at Ashadze 2 (800 x 450 m) the N-S trending trough appears bounded to the east by a faulted gabbroic body. To the west, it is limited by a narrow N-S trending ridge, 20 to 50 m-high, that bears numerous extinct hydrothermal chimneys (Ondreas et al., 2007). Ashadze is the deepest known hydrothermal system and the only site located on the western slope of the MAR rift valley; all others occur on the eastern slope or in the axial part of the rift valley.

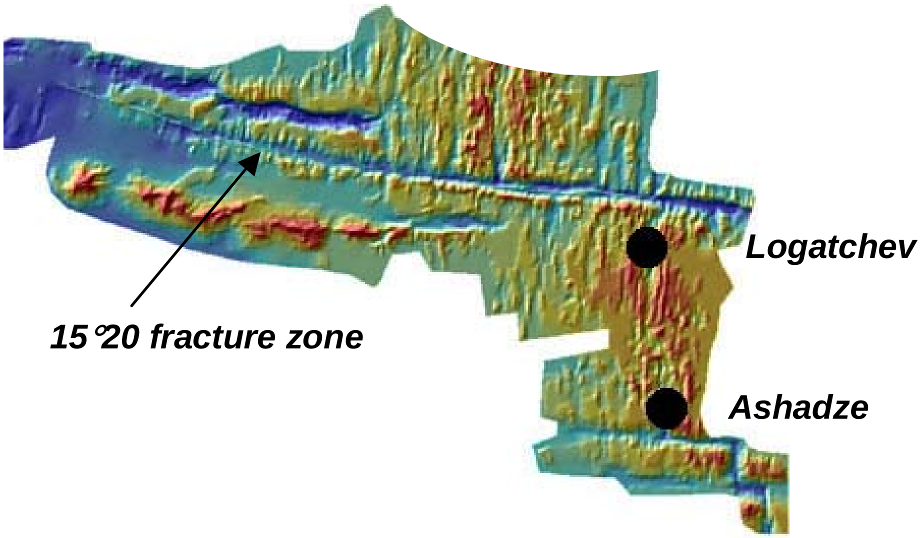


Figure 8: Location of the Logatchev and Ashadze hydrothermal field south of the 15°20 fracture zone, on the MAR axis. (Modified after Hélène Ondréas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Serpentine cruise, 2007, Ifremer)

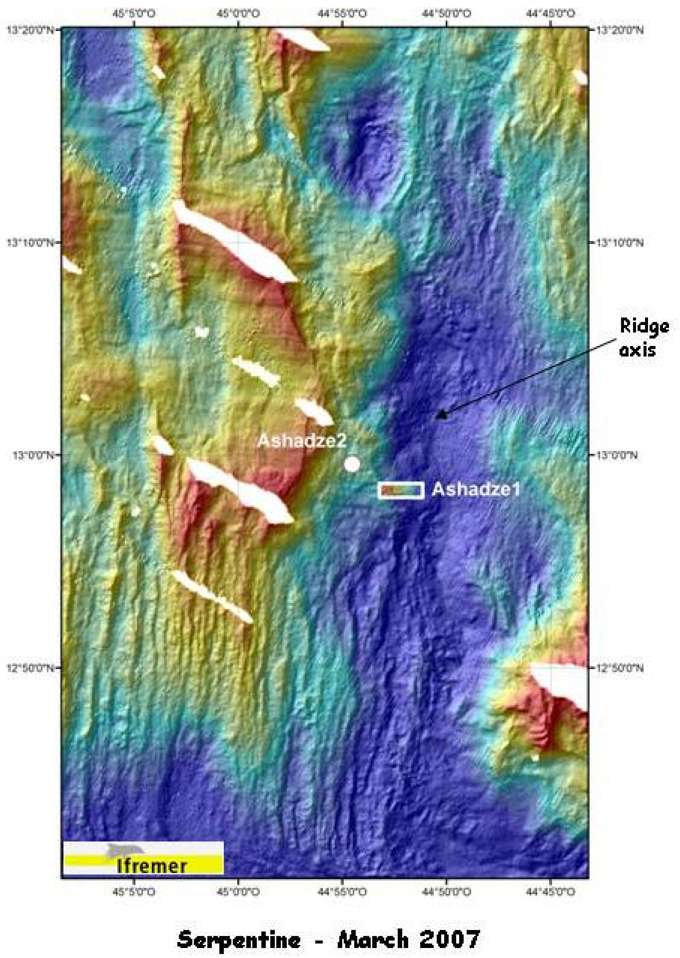


Figure 9: Detailed bathymetric map around the Ashadze hydrothermal field and location of the sites Ashadze1 and Ashadze 2. (Modified after Hélène Ondréas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Serpentine cruise, 2007, Ifremer)

3.3.2 Logatchev

The ultramafic-hosted Logatchev hydrothermal field occurs just south of the fifteen-twenty fracture zone of the MAR, on the eastern rift ***(Figure 8)***. The existence of this field had been postulated since 1990 but was only discovered in 1994 (Batuev et al., 1994). It consists of 3 sites: Logatchev 1, Logatchev 2 and Logatchev hill. Logatchev 1 (14°45'N and 3000 m) has been visited many times and is well documented (Schmidt et al., 2007; Petersen et al., 2009). The hydrothermal activity at the two other sites was discovered and sampled by Ifremer during the SERPENTINE cruise in March 2007. Both Logatchev 1 and 2 are located off-axis (8 and 12 km respectively) and lie to the north of a small offset axial discontinuity, in an inward position relative to fossil corrugated surfaces.

Logatchev 1 consists in 9 sites distributed on a NW to SE axis (50 - 200 m between each) over a distance of about 600 m ***(Figure 10)***. The fluid inorganic composition from all vents is similar indicating a single source, however they show very different morphologies. While sites Irina II and site A are mound-like structures with 1 to 5 m high black smokers chimneys on top, Quest, site B, Irina I and Anna Louise are so-called smocking craters which can be described as donut-shaped positive topographic features with a 1 to >5 m crater rim developed above the surrounding seafloor and a 2-5 m deep central depression (Petersen et al., 2009). These craters are very characteristic of the Logatchev field although they are also reported at the Ashadze field (Fouquet et al., 2008). Another particularity of the Logatchev 1 system is the extremely copper and gold enrichment of massive sulfides (Gablina et al., 2000); this co-enrichment is unusual on the modern seafloor (Hannington et al., 2005).

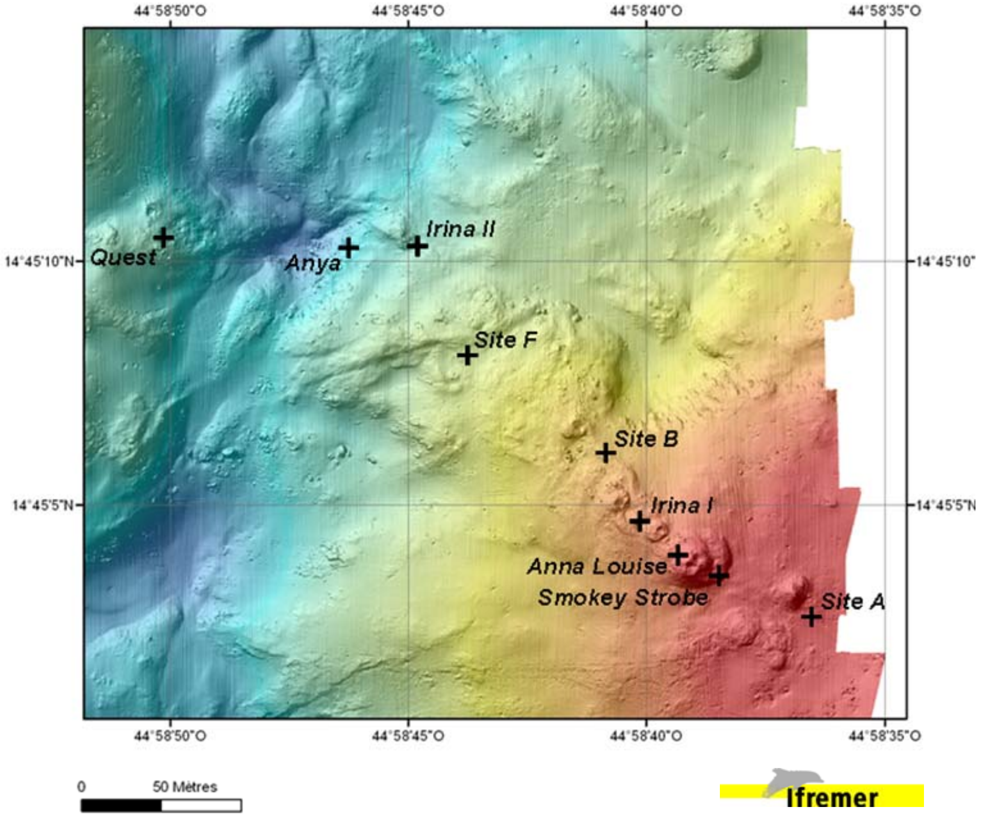


Figure 10: Detailed bathymetric map of the Logatchev 1 site and location of the active vents. (Modified after Hélène Ondréas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Dive 315 - Serpentine cruise, 2007, Ifremer)

4 H_2 generation during serpentinisation

Serpentinised ultramafic rocks have received considerable attention as a source of H_2 for hydrogen-based microbial communities e.g. (Alt and Shanks, 1998; Takai et al., 2004) and as a potential environment for the abiotic synthesis of methane and other organic compounds within the Earth’s crust through reduction of CO_2 or CO by H_2 e.g. (Berndt et al., 1996; Shock and Schulte, 1998; Charlou et al., 2002; McCollom and Seewald, 2007; Konn et al., 2009). Both these processes rely on the development of strongly reducing conditions and the generation of H_2 during serpentinisation.

Serpentinites are produced by hydrous alteration of ultramafic rocks, primarily peridotites which are mainly composed of the minerals olivine and pyroxene. Although the minerals are thermodynamically stable in the presence of water at elevated pressures and temperatures in the mantle, they become unstable when exposed to lower temperatures in the near surface environment and undergo reaction with water. This reaction typically results in a mineral assemblage dominated by serpentine, along with magnetite, brucite or talc. Generation of H_2 during serpentinisation results from the reaction of water with ferrous iron (Fe^{II}) mainly derived from olivine and pyroxene. In the reaction, Fe^{II} is oxidised to Fe^{III} (ferric iron), which typically precipitates as magnetite (Fe_3O_4) while hydrogen from water is reduced to H_2. However, much of the Fe^{II} released during serpentinisation winds up in serpentine and brucite solid solutions rather than in magnetite. Since Fe^{II} that partitions into these solid solutions is not available for oxidation to Fe^{III} in magnetite, the amount of H_2 produced will decrease. Various factors such as temperature, water:rock (W:R) ratio, reactant rock and fluid composition may influence the partitioning of ferrous iron. In turn the partitioning will affect the amount and production rates of H_2. In a recent study, McCollom and Bach (2009) tackled these intricacies by exploring thermodynamic constraints on fluids and mineral composition during serpentinisation using a reaction path model rather than a phase equilibrium model.

4.1 Influence of temperature

Temperature was found to be the most critical factor affecting the H_2 production as it has a particularly large impact on the proportion of Fe^{II} that precipitates as a component of brucite. According to McCollom and Bach’s model, H_2 concentration would attain a peak at 315°C for

W:R = 1. At temperatures below 315°C, olivine is unstable and serpentine is the dominant mineral occurring along with brucite and magnetite. As temperature decreases, Fe^{II} (as $Fe(OH)_2$) is preferentially incorporated into brucite rather that magnetite, explaining the decrease in H_2 concentrations. At temperatures above 315°C, olivine becomes stable and the generation of H_2 is limited by attainment of thermodynamic equilibrium resulting in partially reacted olivine and thus decreasing the amount of Fe converted to magnetite. At temperatures above 370°C, although olivine becomes essentially unreactive, H_2 is still produced via alteration of pyroxenes. (***Figure 11***)

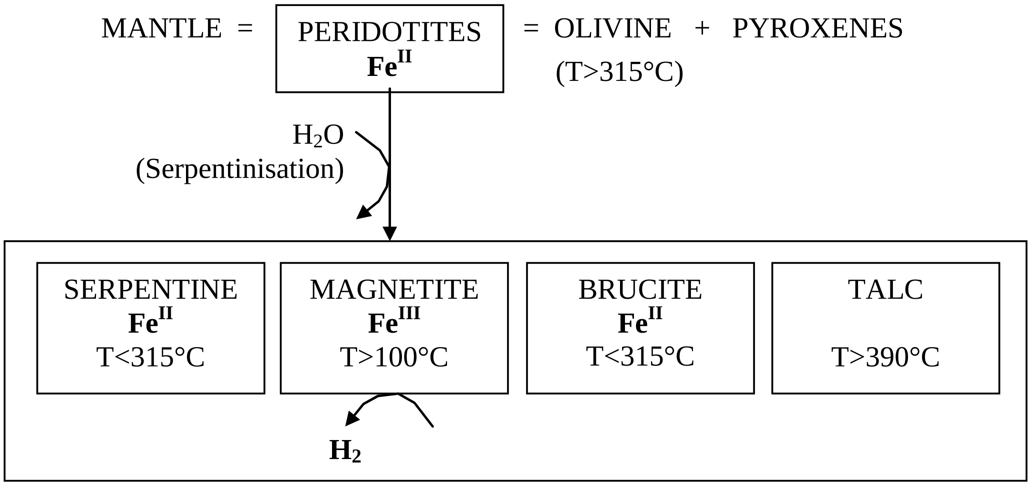


Figure 11: Schematic of the serpentinisation reaction. It produces different minerals depending on the temperature. For each mineral the temperature above or under which it is stable is given. The schematic highlights the fact that only the conversion of Fe^{II} to Fe^{III} produces H_2.

4.2 Influence of water:rock ratio

W:R ratio was reported to also influence the Fe content of brucite somewhat, but the impact of this factor seems to be relatively minor (McCollom and Bach, 2009). Whatever the temperature, at low W:R water is incorporated into hydrated alteration minerals at equilibrium leading to a decrease of the amount of liquid water and thus a steep concentration increase of any dissolved compound. Therefore concentrations of H_2 will always be higher at low W:R than at high W:R despite a higher production of H_2 per kg of rock (diluted in more water). Even at high W:R the concentrations of H_2 at 300°C were higher than the highest concentrations obtained at low W:R at 100°C, which is due to the fact that Fe partition more into magnetite at 300°C than at 100°C (see above section) so that the overall H_2 production is higher. At 350°C, the variation in the H_2 production with W:R followed the same pattern like at 300°C but concentrations were always lower than at 300°C for a given W:R, because at 350°C olivine is only partially reacted and less water is incorporated in alteration minerals. Finally, the model predicts the highest concentration of H_2 at 300°C and very low W:R, however such concentrations cannot be reached because they exceed the solubility of H_2 and the accumulation of H_2 is limited in any case by the formation of native metals, particularly Fe-bearing alloys. As a result, the authors concluded that H_2 concentrations to during serpentinisation at temperatures around 300°C and low W:R ratio may level off at approximately 400 mmolal.

4.3 Other influencing factors

Other parameters are likely to affect the generation of H_2 during serpentinisation. Particularly at low temperatures kinetic factors would further limit rates of H_2 production. At temperatures >~200°C reaction rates are sufficiently rapid that extensive serpentinisation can occur on time scale of a 1000 years or less. On the contrary, substantially longer timescales would be required for serpentinisation to proceed at lower temperatures, so that in natural environment the residence time of the fluid is likely to be an additional limiting factor of the H_2 production.

4.4 Implications for H_2-based microbial communities and abiotic synthesis

In environments with temperatures low enough to sustain microbial communities (<120°C), the model indicates that partitioning of Fe into brucite may significantly restrict the amount of H_2 to be produced. In addition, serpentinisation kinetics is very slow at low temperature. Combining these effects and considering that the strongly alkaline conditions attained during low temperature serpentinisation may impose steep metabolic costs or nutrient limitation, environments in contact with end member (unmixed, pure) hydrothermal fluids could be very challenging places for hydrogen-consuming bacteria to inhabit. Nevertheless, at Lost City, which is a naturally occurring example of the above described conditions, hydrogenotrophs constitute the majority of archaea (a type of micro-organism) found in the warm interior of carbonate chimneys in contact with the hot end member fluids (Boetius, 2005)

Hydrogen concentrations recorded in fluids from the Rainbow, Logatchev and Ashadze ultramafic-hosted hydrothermal fields are in the 10-26 mM range (Charlou et al., InPress) and their measured venting temperature (350-365°C) suggest that they could be in a regime where olivine is reactive. However, the fluids may have cooled during ascent to the surface and temperatures within subsurface reaction zones have been suggested to be as high as 400 at Rainbow (Charlou et al., 2002; Allen and Seyfried, 2003). In the 350 - 400°C range of temperature olivine is stable and the fluid-rock interactions that partly control the fluid composition in these systems would favourably lead to the formation of talc, tremolite and magnetite rather than serpentine (section 4.1 and ***Figure 11***); which would constrain H_2 concentration to lower values than field measurements. According to the model, to explain the concentration of H_2 observed, serpentinisation reaction zones would need to have lower temperatures where olivine becomes unstable. At the Lost City hydrothermal field, low venting temperatures (40-91°C) co-exists with high hydrogen concentrations (up to 15 mM) (Kelley et al., 2001; 2005). In any case, serpentinisation reactions taking place at these low temperatures can be accounted for such great H_2 production hydrothermal fluids. Therefore it has been proposed that serpentinisation may occur at higher temperature in the subsurface where the heat would be derived from both serpentinisation and magmatic dike input (Allen and Seyfried, 2004). Up to date, suggested subsurface reaction zone temperatures are in the range 110-200°C (Allen and Seyfried, 2003; Proskurowski et al., 2006), but even these temperatures are too low for serpentinisation to generate up to 15mM of H_2 according to the model of McCollom and Bach (2009). Serpentinisation may definitely be the sole process responsible for the entire production of H_2 in ultramafic-hosted hydrothermal systems considering that the model of McCollom and Bach (2009) predicts concentrations of H_2, potentially attaining values an order of magnitude or more higher than current field observations (10-26mM), would be reached at ~300-325°C. Nevertheless, one cannot disregard the possible occurrence of other H_2 generating processes.

Serpentinite-derived fluids are commonly observed to have high abundances of methane and other light hydrocarbons (Berndt et al., 1996; Shock and Schulte, 1998; Charlou et al., 2002; McCollom and Seewald, 2007) as well as lower abundance of heavier hydrocarbons and other organic compounds (Konn et al., 2009). Hydrocarbons have been suggested to be abiotically derived from the reaction of H_2 with CO_2, which would be favourable under high H_2 concentrations. According to the model predictions, ultramafic rocks undergoing alteration in the 200-315°C should generate the greatest amounts of H_2 and would therefore appear to have the greatest potential as environments for abiotic organic synthesis.

5 Inorganic composition: affecting factors

Clear variations exist in the pH values as well as in the element and gas compositions of hydrothermal fluids, both between mafic- and ultramafic-derived fluids, and among fluids discharged from serpentines. These observations raise the question of what controls the final inorganic composition of these fluids. The journey of a hydrothermal fluid can be schematised as follows: cold seawater is progressively heated when it penetrates the crust through faults (recharge phase). The first interactions with the rocks result in depletion of the fluid in magnesium and sulfate and enrichment in hydrogen sulfide. The fluid then reaches a maximum temperature in the high-temperature reaction zone, close to the heat source (typically a magma chamber 1-2 km below seafloor for mafic-hosted systems and probably deeper for ultramafic-hosted systems). The fluid slowly cools by conduction and possibly by mixing with seawater in local recharge zones in the vicinity of the chimney affecting its final inorganic composition. To be noted, one characteristic feature common to all unmixed hydrothermal fluids from ultramafic-hosted systems is the total absence of magnesium. Mg is indeed efficiently removed from hot seawater and precipitated during rock alteration and thus pure hydrothermal fluids are considered to be Mg-free (Mottl and Holland, 1978). Practically, the concentration of Mg is the criteria to asses the purity of a given hydrothermal fluid, i.e. the proportion of seawater mixing. The measured concentration values are then extrapolated to values at zero magnesium concentration. These extrapolated values are called end member values and characterise the fluid.

The mineral composition of the host-rocks where alteration reactions take place is one of the major factors influencing the inorganic composition of the fluids as they exchange various elements with the minerals whilst altering them. However, the inorganic composition of the fluids is also strongly influenced by hydrothermal alteration processes themselves, which in turn are very much controlled by pressure and temperature. In addition, other factors such as phase separation, W:R ratio and residence time (i.e. how long the fluid stays in contact with the rocks) may also have an impact.

5.1 Lithologies and alteration processes

Typically, basalt-derived fluids are characterized by relatively low amount of H_2 and CH_4, high H_2S and silica concentration and enrichment in Light Rare Earth Elements (LREE) as well as magmatic volatiles such as CO_2 (Douville et al., 2002). Whereas, high concentrations of reduced gases (H_2 and CH_4), low H_2S concentration as well as low silica and potassium contents, enrichment in Li vs. basalt-derived fluids and depletion in B compared to surrounding deep seawater are indicative of serpentinites-seawater interactions.

Also strong variations of the fluid chemistry are observed among ultramafic-hosted hydrothermal systems of the MAR (***Table 1***). One of the most striking differences is maybe the high pH observed at the Lost City hydrothermal field in comparison to all other known ultramafic-hosted hydrothermal systems. The correlation between pH and temperature at Lost City is consistent with calculations predicting that peridotites-seawater interaction should lead to high pH especially at low temperature (Wetzel and Shock, 2000; McCollom and Bach, 2009). Typically, for W:R=1, pH~10 at 100°C and pH~6 at 400°C. However, the models also show that pH is partly driven by the mineral composition of the host-rock at thermodynamic equilibrium, for instance, with pyroxenes leading to lower pH than olivine.

Various alteration pathways are possible at the seafloor: for example melt/rock interaction of serpentinites and mafic intrusions, low temperature weathering and serpentinisation are suggested alteration pathways for the Logatchev hydrothermal system (Augustin et al., 2008). Whether these processes occur simultaneously or discretely will probably result in distinct inorganic signature to the fluids.

5.2 Temperature, pressure, residence time and water:rock ratio

The thermodynamic stability of the mineral phases contained in the host-rocks is crucial as it dictates the minerals to be altered by a given water-rock reaction and also is the thermodynamic stability of the alteration products. It appears that thermodynamic stability is mostly affected by temperature whereas relatively insensitive to pressure. Finally, only large variations in W:R ratio (1 to 2 order of magnitude) seem to somewhat influence the mineral thermodynamic stability at a given temperature (McCollom and Bach, 2009).

In the case of a thermodynamically favourable alteration process but limited by kinetics factors, one can easily understand that the longer the fluid will interact with the rock, the more chance the reaction has to proceed, in other words the residence time may influence chemical equilibria, thus the resulting products and the composition of the circulating fluid.

By contrast, W:R ratio has a strong impact on concentration of elements in hydrothermal fluids. At low W:R a large fraction of the water is incorporated into hydrated alteration minerals at equilibrium. As a result, the amount of fluid within the rocks decreases and the concentration of dissolved compounds, especially Cl^-, dramatically increases in the remaining fluid without, of course, exceeding solubility values.

5.3 Phase separation

Phase separation of circulating fluids has been suggested to occur in ultramafic-hosted hydrothermal systems because salinities greatly higher (up to 780 mM of Cl^-) as well as greatly lower (down to 170 mM of Cl^-) than deep seawater background value (545 mM of Cl^-) were observed (Charlou et al., 2002; Koschinsky et al., 2008; Charlou et al., InPress). At conditions near or above the critical point (T_c = 407 °C, P_c = 298 bar), seawater occurs as two co-existing phases (a vapour phase and a brine phase) in which metals and other elements will partition. Experimental work demonstrated that partition was zero at the critical point and increased with greater density difference (density increases above the critical point CP) (Pokrovski et al., 2005). Elsewhere, Bischoff and Rosenbauer (1987) have shown that phase separation leads to acidity and heavy metal concentrations increase in the chloride-rich phase. Metals such as Fe, Ni and Zn are known indeed to form complexes with Cl, especially favoured at low pH, high temperatures and low water density (Ding and Seyfried Jr, 1992), resulting in a similar partitioning of these metals to Cl. However, some other metals such as Cu seem to favour sulfide complexation so that they would preferentially partition into the vapour phase (Nagaseki and Hayashi, 2008). Finally, Koschinsky et al. (2008) reported an enrichment of Co and Mo in low salinity phase-separated fluids, which may indicate that these metals do not form complexes with Cl as their partitioning do not follow the same trend than Cl partitioning. For a more detailed approach on the phase separation process at submarine hydrothermal systems, we refer to a recent review by Foustoukos and Seyfried (2007).

6 Organic geochemistry - pathways

As discussed in the previous sections, the processes controlling the inorganic chemistry of the fluids circulating within the Earth’s crust are numerous and not well constrained and/or understood; and neither are the processes controlling the organic chemistry of the fluids. Both the sources of the building units composing organic molecules (C, H, O and N) and possible reaction pathways leading to organic compounds are multiple, therefore determining the origin of organic compounds and understanding their formation appears a real challenge. On the one hand rocks, minerals and seawater are potential C, H, O and N sources; in a simplified view, CO_2 and carbonates for C, H_2 and water for H, N_2 and NH_3 for N, water and oxygen-bearing minerals for O. On the other hand, micro-organisms that inhabit hydrothermal vents and the subsurface may provide with C, H, O and N by two ways: (i) direct production of simple molecules (typically, CH_4, H_2, acetate, CO_2), (ii) thermal degradation of the micro-organisms themselves if exposed to too high temperature. In addition, macro-organisms may also undergo thermal degradation after death and sedimentation. Whether C, H, O, N are derived from rocks, minerals and seawater or from organisms, they will be referred to abiogenic or biogenic, respectively. Similarly, abiotic processes represent any purely chemical processes, biogenic processes encompass all reactions driven by micro-organism and thermogenic processes refer to thermal degradation of larger organic molecules (proteins, cellulose, etc…) to smaller and simpler ones. Reaction pathways that may produce organic compounds in hydrothermal systems are likely to use both biogenic and abiogenic C, H, O and N. Besides cracking, recombination and rearrangement of primary produced organic molecules is likely to occur under hydrothermal conditions, leading to additional mixing of biogenic and abiogenic C, H, O and N elements within larger organic compound (> 3 carbon atoms). As a result, our ability to clearly classify organic compounds, other than CH_4 and acetate, into the biogenic or abiogenic category seems to be compromised.

6.1 Abiotic processes

Abiotic synthesis will only occur if the thermodynamics are favourable and this has been shown to be the case for a wide range of organic compounds under conditions found at modern subseafloor hydrothermal (e.g. Shock, 1990; McCollom and Seewald, 2001); especially hydrocarbons and amino acids for which specific reaction pathways have been proposed. The hypothesis is that organic compounds would occur in metastable equilibrium thanks to kinetic barriers that would prevent the inherently sluggish stable equilibria CO_2/CH_4 and N_2/NH_3 to establish in hydrothermal solutions. I refer to paper I (Konn et al., 2009) for a more in depth discussion.

6.1.1 Fischer-Tropsch Type reactions (FTT)

Abiogenic synthesis of hydrocarbons has been discussed since 1940 (Glasby, 2006). Many approaches have been described and even though researchers have still not come to a conclusion, it is generally accepted that hydrocarbons could be generated by reduction of CO_2 via an aqueous Fischer-Tropsch Type (FTT) reaction. The Fischer-Tropsch reaction is a common industrial process, which was invented by two German scientists, Franz Fischer and Hans Tropsch, in the 1920s. The mass balance equation (3) is as follows:

$$(2n+1)\ H_2 + nCO \rightarrow C_nH_{2n+2} + n\ H_2O \tag{3}$$

The reaction requires catalysis. Typically iron or cobalt bearing catalysts are used for industrial processes. The industrial reaction is not specific. It converts carbon monoxide CO and hydrogen H_2 into a wide range of liquid hydrocarbons that need to be further refined in order to obtain, for instance, synthetic fuels. The process was mainly used in World War II by Germany and Japan to produce substitute fuels and has since been improved. It is still subject to current research and Fischer-Tropsch reactions nowadays refer to a wide range of surface catalyzed reactions. To be noted, the first step of the Fischer-Tropsch reaction (n=1) is called the Sabatier reaction and generates only methane (CH_4).

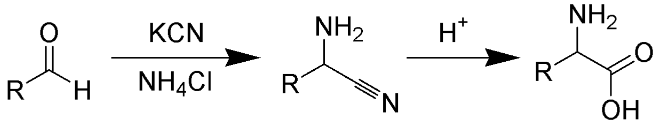
Carbon sources other than CO can be utilized and the reaction will still occur. In hydrothermal systems, CO_2 is the most likely reactant and numerous laboratory experiments (McCollom et al., 1999; McCollom and Simoneit, 1999; McCollom, 2000; Rushdi and Simoneit, 2001, 2004, 2005, 2006; Seewald et al., 2006) have shown that saturated hydrocarbons as well as other organic compounds can be abiotically produced via FTT reactions under hydrothermal conditions, with CO_2 as an indirect carbon source. Besides, it is suggested that the first stage of the FTT reaction, in that case, would be the formation of CO via reduction of CO_2 by H_2 (4):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{4}$$

Finally, linear hydrocarbons have been detected in fluids from ultramafic-hosted hydrothermal systems and are likely to derive from FTT reactions (Konn et al., 2009; Paper II; Paper III).

6.1.2 Strecker-type synthesis

The abiotic synthesis of amino acid are of particular interest in the origin of life question as they represent the fundamental building blocks of proteins that are required for the development of living organisms and it has been generally proposed to occur via a Strecker-type mechanism under hydrothermal condition. The original Strecker amino acid synthesis, devised by Adolph Strecker in 1850, is a series of chemical reactions that synthesize an amino acid from an aldehyde (or ketone) according to reaction (5):



(5)

The Strecker-type synthesis has been shown to be thermodynamically favourable over all ranges of temperatures appropriate for a hydrothermal system at 300 bar (Brandes et al., 1998). Nevertheless, for this reaction pathway to proceed in hydrothermal systems reduction of inorganic carbon (CO or CO_2) and nitrogen (N_2) must precede to form the required reactants (HCN and aldehyde or ketone) (Holm and Neubeck, 2009). This is both experimentally and thermodynamically favoured at high hydrogen concentrations. As for the reactants, both thermodynamics and experimental work strongly support their possible formation in hydrothermal systems. Preliminary results suggest the occurrence of amino acids in hydrothermal fluids from ultramafic-hosted hydrothermal vents, however their origin has not yet been investigated (Paper IV).

6.2 Biogenic processes

Chemolitotroph microbial communities commonly colonize hydrothermal vents and may represent analogs for life on the early Earth and other planets. Chemolitotrophic organisms, by definition, utilize only inorganic simple molecules for their carbon and energy source so that they do not rely on other living organisms to feed, develop and multiply. Up to date the maximum temperature for some of such organism to live is 120°C.

In our case, the archaea methanogens, which are one of the most common micro-organism groups found at hydrothermal vents, are of particular interest as they synthesize CH_4 from CO_2

and H_2. The consumption of methane by methanotrophic bacteria also occur, although to a less extent as methanotrophs are less abundant in hydrothermal environments, and lead to the production of CO_2. Also from CO_2 and H_2, acetogenic bacteria are able to generate acetate.

This biogenic methane, carbon dioxide and acetate could well then be involved in abiotic processes that generates heavier organic compounds such as the previously described FTT and Strecker-type reactions. Hydrocarbons could also be abiotically synthesized via methane surface polymerisation but from biogenic methane. The question is: “What shall we call those resulting organic compounds?” They are neither biogenic, nor abiogenic nor thermogenic. In any case they are potential precursor of life as their formation relies on biogenic primary reactants.

6.3 Thermogenic processes

Thermogenic processes refer to any thermal degradation (cracking) of any type of biologically-derived matter. Typically, thermogenic processes occur in sedimentary basins and are associated with maturation of petroleum. Oil indeed results of the slow decomposition process under heat and pressure of ancient sedimented fragments of plants and organisms. This sediments supply is limited and therefore oil is called fossil-fuel by opposition to renewable energy. Hydrothermal systems definitely meet the condition of high pressure and high temperature required for thermal degradation. Besides, organic matter is present in the form of macro-organisms and micro-organisms thriving both around the chimneys and in the subsurface. Macro-organisms will inevitably die and fall on the seafloor. This may be followed by partial bacterial decomposition. Degradation products may be taken up by seawater and penetrate the crust in the recharge zone of hydrothermal systems and thus undergo thermogenesis deeper in the crust. Similarly, microbial organisms that thrive in the subsurface may be either flushed by a cold fluid and carried away to a zone in the crust where temperature would be high enough to degrade the very strong lipids forming the membranes of the bacteria and archaea; or burned off as a very hot fluid would encounter these organisms. To test this hypothesis, in other words to investigate the organic signature resulting from thermal degradation of such micro-organisms, a hydrothermal degradation experiment of a thermophile archaea biomass was carried out and was the purpose of (Paper III).

6.4 Supercritical water chemistry

Everyone has observed water in its solid, liquid and vapour phase as well as everyone has physically experienced the transitions between solid and liquid (melting and freezing) and liquid and vapour (condensation and vaporisation). Because it requires specific pressure - temperature combinations which are not commonly encountered on Earth, it is less frequent to observe sublimation or deposition i.e. when solid becomes gas and vice versa without transit by a liquid phase. Even more difficult to obtain is the co-existence of the three phases which occur at the triple point; one very particular combination of pressure and temperature. Another important point is the critical point which occurs at elevated pressures and temperatures (***Figure 12***). The critical point specifies the temperature and pressure conditions at which a phase boundary ceases to exist i.e. at which the densities of the vapour and the liquid phases are equal. The equilibrium system is a homogeneous supercritical fluid.

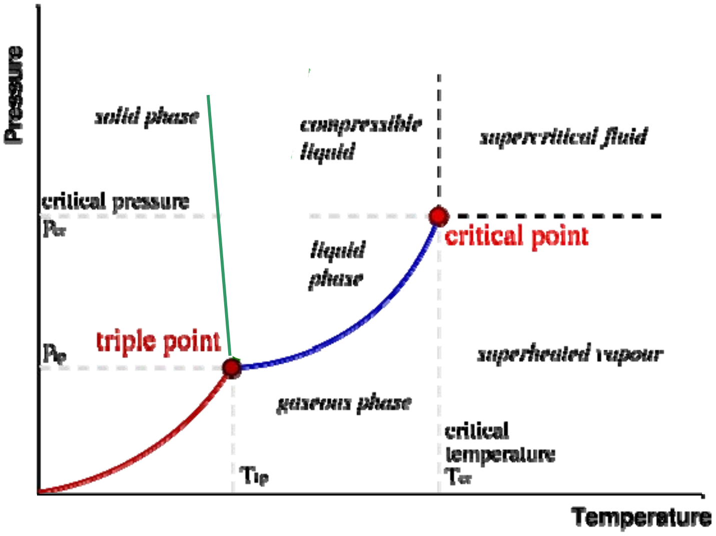


Figure 12: Phase diagram of water. Modified after http://en.wikipedia.org/wiki/File:Phase-diag2.svg.

Conditions near and above the seawater critical point (Tc = 407 °C, Pc = 29.8 MPa) are frequently encountered in hydrothermal systems and especially fluids from almost all ultramafic-hosted hydrothermal systems have been shown to reach supercritical state (Charlou et al., InPress). Dramatic changes in the physical and chemical properties of water occur as temperature increases. Large variations in density, dielectric constant, solubility parameter and ionic product are observed. As a result, the solvent properties of water at high temperatures are similar to those of polar organic solvents at room temperature, thus facilitating reactions with organic compounds. Organic molecules that were previously considered to be unreactive in liquid water undergo many chemical reactions when the temperature is increased to 250 - 350°C. Supercritical water becomes an excellent solvent for ionic condensations, cleavages, hydrolysis, oxidations, hydrogenations and hydroformylations. The role of water can be multiple: solvent, reactant, catalyst, proton donor, complexation agent and hydration agent have been proposed. Finally, the main reaction pathways that have been identified so far in supercritical water are those with an ionic or radical character, which seem to occur in distinct zones of the P-ρ-T (with ρ the density) surface diagram of water and to compete in the vicinity of the critical point (Watanabe et al., 2004). Additionally, molecular rearrangements, which are reactions in which neither radical nor ionic intermediates are involved, possibly proceed around the critical region of water (Akiya and Savage, 2002). Unfortunately exact reaction pathways and kinetics occurring in supercritical water are unknown and largely uncharacterised (Peterson et al., 2008), therefore a wide variety of reaction pathways are certainly left to be investigated for the formation of amino acids and other organic compounds in hydrothermal systems.

7 Discussion

7.1 Are modern submarine hydrothermal vents representative to early Earth conditions?

It is commonly agreed that life would have appeared on Earth in the earliest Archean or even before (Russell and Hall, 1997; Rosing, 1999). The Archean Eon spreads from 3.8 to 2.5 billion years (by) or Giga années (Ga). The preceding Eon is called Hadean. Figure 13 shows portion of the geological scale related to those periods and summarises the major events that occurred on Earth at that time.

First and foremost if one assumes that life could have originated in hydrothermal systems on early Earth, it should be mentioned that hydrothermal activity is relevant to Hadean and Archean Earth as it began as soon as water condensed to form oceans and some kind of plate tectonics (corresponding to crust formation) appeared i.e. 4.4 Ga ago (Wilde et al., 2001). Also hydrothermal systems as well as ultramafic rocks were much more abundant on the primitive Earth than today (Russell et al., 1988) as well as ultramafic rocks were. Second, one should assess the relevance of the conditions occurring at modern submarine hydrothermal systems to the early Earth's conditions, i.e. Archean conditions.

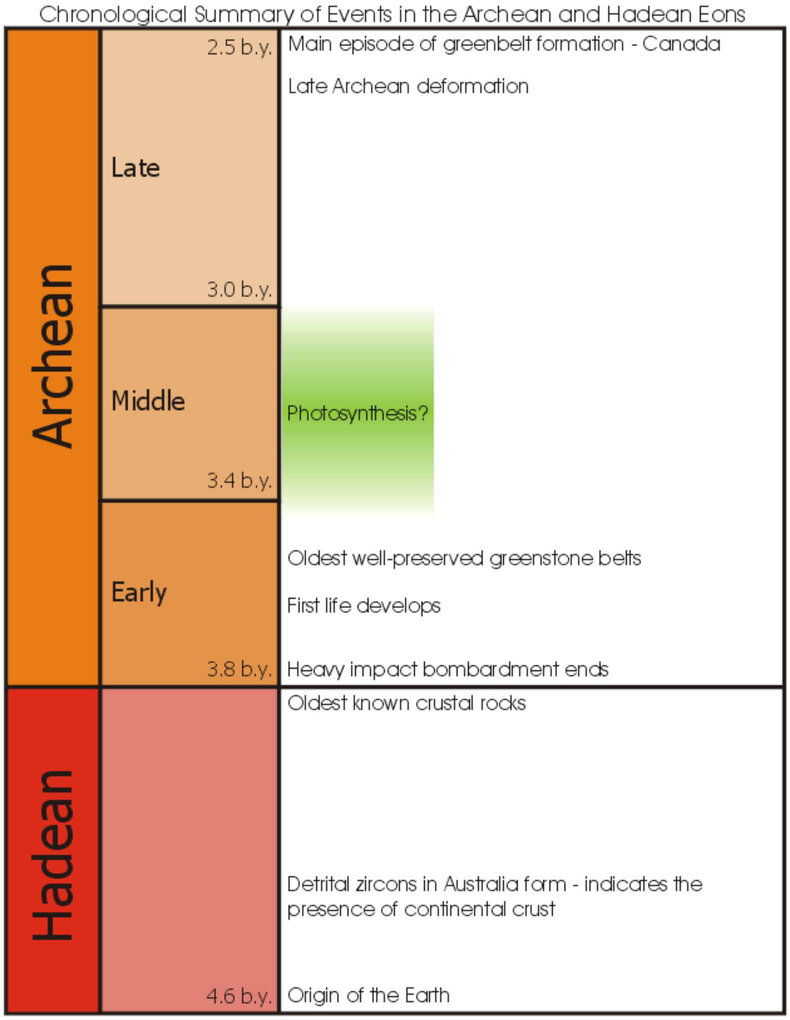


Figure 13: History column and major events in the Hadean - Archean Eons. To be noted the date of apparition of photosynthesis is subject to current debate (Allwood et al., 2009). From Winona State University website http://www.winona.edu/geology/MRW/mrwimages/ArcheanHistoryColumn.gif

Although the composition, oxidation state, the temperature and the pressure of the early atmosphere after the bombardment is unknown (e.g. Marshall, 1994; Schoonen et al., 1999), a proposed composition on which most of the scientific community agrees on is mainly CO_2, N_2, H_2O and little amount of H_2S with CO_2 being in a dense state (Chen and Chen, 2005). Others have suggested CO to have been more abundant than generally accepted and partial pressure of CO in the atmosphere could have reached up to 0.06 atm (Abelson, 1966; Kasting, 1990). Moreover, the early atmosphere may have also contained small amounts of HCl, SO_2 and elemental sulphur S^0 and minor amounts of H_2 and Ar (Russell and Arndt, 2005). Finally, different lines of evidences indicate the presence of CH_4 in the atmosphere in the Archean.

Significant levels (100-1000 ppm) probably compensated for the lower luminosity of the sun and kept Earth from freezing and may have been reached in the late Archean (Pavlov et al., 2000; Kasting, 2005). Fiebig and coworkers (2007) proposed an abiogenic origin of this CH_4 and estimated fluxes to be in the 40-80Mt/year range in the Archean.

Mantle degassing of nitrogen in the Hadean was probably more vigorous than today, therefore the ocean would have been richer in nitrogen which would have essentially occurred as N_2 and NO (oxidized forms, (Martin et al., 2007; Ducluzeau et al., 2009)) with very little of ammonia (reduced form) (Kasting, 1990; Schoonen and Xu, 2001). The oceanic concentration of CO_2 appears difficult to estimate on early Earth, however CO_2 was definitely present in the ocean via dissolution of atmospheric CO_2 (Russell and Arndt, 2005). Similarly, small amount of dissolved CO may be expected in the early ocean. Magnesium (Mg) as well as transition metals such as iron (Fe), nickel (Ni) must have been abundant in the early ocean (Huber and Wächtershäuser, 2006). Mg^{2+} together with Ca^{2+} would have been the prevalent divalent cation whilst the prevalent monovalent cation being Na^+ (Pontes-Buarque et al., 2000). Finally, the ocean is considered to have been fairly acidic with a pH ~ 5-6 (Russell and Arndt, 2005).

Almost uncontested, up to date, is the view that both atmosphere and ocean would have remained anoxic (oxygen free) until the great oxidizing event postulated at 2.4 Ga ago. However, several controversial lines of evidence, including the sulphur isotopic composition of pyrites and the elemental compositions of ancient soils horizons, have been put forth to support instead the presence of appreciable amounts, or at least whiffs of oceanic and atmospheric oxygen long before (Anbar et al., 2007; Konhauser, 2009). Moreover, a recent paper by Hoashi et al. (2009) reports on the observation of haematite crystals in marine sediments of 3.46 Ga which indicates that free oxygen would have existed in the oceans at that time.

As a conclusion, conditions at modern seafloor hydrothermal systems seem to be similar, to some extent, to early Earth's conditions and thus can be considered place of primary focus in the search for the origin of life. Moreover, hydrothermal vents constitute very favourable environments as much in terms of protection against sterilizing effect of giant impacts (***Figure 13***) as in terms of scale. On the one hand, microenvironments such as mineral surface that favour, via adsorption, concentration of organics and reactions. On the other hand, at the scale of the hydrothermal mound, the system provides with physicochemical gradients and nonequilibrium conditions that are required for the emergence of a living organism (Russell and Hall, 1997;

Kompanichenko, 2009). Notably alkaline (high pH) hydrothermal systems are thought to be even more relevant to Archean hydrothermal vents and the Lost City Hydrothermal field could provide particular insights into past mantle geochemistry and present a better understanding of the chemical constraints that existed during the evolutionary transition from geochemical to biochemical processes. Elsewhere, a complete and strong scenario of prebiotic chemistry resulting in the emergence of life has been described by Russell and coworkers (Russell et al., 2005). Finally, methane would even have been already abiotically produced within Archean hydrothermal vents exactly as it is today (Fiebig et al., 2009).

7.2 Prebiotic molecules, what's next?

Despite abiotic synthesis of organic compounds would have provided prebiotic molecules, i.e. material for life to start (Ferris, 1992; Simoneit, 1995), the majority of macromolecules typical of the cell organization are degraded under such conditions. This highlights the fact that the reactor where prebiotic molecules would have formed has to be different from the one where life has developed i.e. in milder conditions or under some kind of protection in niches. Two main schools coexist in terms of what is crucial for life to start: the RNA world and the membrane world. In the first case, self-replication is considered to be the critical point and it is postulated that RNA or structures that were precursors of RNA are required. In the other case, proponents see that concentration and protection of prebiotic molecules are primordial for the origin of life.

I refer to a review paper of Ferris (2005) for a holistic approach of the RNA theory and for references therein. RNA is a biopolymer which is made of monomers (nucleotides) linked together. A nucleotide is made of a nitrogen base (purines: adenine and guanine and pyrimidines: uracil and cytosine), a sugar (ribose) and a phosphate group. Prebiotic synthesis of the nitrogen bases and ribose has been shown to be possible under hydrothermal experimental conditions and phosphate was likely to occur on the early Earth. Elsewhere, Martin and Russell (2007) discussed in depth, in terms of protometabolic, biochemical and energetic aspects, the origin of all the units that make up an RNA world in an alkaline hydrothermal vent, which appeared to be a good model. Nevertheless, how these molecules would have combined to form nucleotides and further RNA remains unclear. Alternatives propose that simpler molecules that were precursors of RNA must have existed (preRNA world); for example polynucleic acids (Nelson et al., 2000). Others postulate that good candidates for RNA precursors are entirely mineral structures capable of self-replication (proto-RNA) (Greenwell and Coveney, 2006). Once RNA or assimilated structures would have been formed it would be capable to self-replicate and life could start (Koonin and Martin, 2005; Lincoln and Joyce, 2009).

The first prebiotic molecules are likely to have been small and simple and to have been produced at low concentration. However, larger molecules such as RNA or proteins are needed for life, which implies that the probability that those molecules meet and react to generate larger organic molecules has to be enhanced. In other words, the existence of structures capable of concentrating the very first material appears of prime importance and this constitutes the core of the second school previously mentioned. One view in this theory is that the structure must have been a membrane type, that would enable leaching and penetration of organics, as the first form of cellular life need a membrane (Deamer et al., 2002). Segré et al. (2001) suggested a lipid world based on the property of lipids to self-assemble (Walde, 2006). Thanks to their amphiphilic character, they would form vesicles in which the small prebiotic molecules could have been enclosed. Chemical reactions could then have occurred in those shelters and delivered the first material for life to start. Finally, amphiphilic molecules such as esters or carboxylic acids have been hydrothermally synthesized in the lab (e.g. McCollom et al., 1999; Rushdi and Simoneit, 2006) and detected in ultramafic-hosted hydrothermal fluids (Konn et al., 2009), which supports the idea that lipid-type vesicles could actually form in hydrothermal systems. A less popular mineral approach was proposed by Ashkabov (2008) and relies on the Quataron hypothesis. Quatarons are a specific form of nanosize cluster self-organisation of matter, typically CH_4 or H_2O are known to form quatarons. They are hollow and the cavities, interestingly, have been found to be of the size of nitrogen bases and phosphate groups. Quatarons are viewed as concentrators of the main biogenic elements and as sites of primary synthesis of biomolecules. They only exist under nonequilibrium conditions and have been shown to form in water vapour and oversaturated vapour (Wilson, 1897; Askhabov, 2008). Quatarons could have thus form in the atmosphere or in supercritical hydrothermal fluids.

7.3 Oil a renewable energy?

Today, the biogenic origin of oil theory prevails and states that all petroleum found in our planet is derived from biological precursors (e.g. Forsman and Hunt, 1958; Eglington and Calvin, 1967; Albrecht and Ourisson, 1971; Moldowan and Seifert, 1979, Tissot, 1984; Summons and

Janhke, 1992). The theory is well proved and supported by laboratory experiments, in which petroleum composition and distribution pattern (i.e. the relative proportions of the different hydrocarbons composing oil) are shown to reflect that of oil generated from kerogene pyrolysis (i.e. organic matter decay). Moreover, oil samples related to sedimentary rocks of a certain depositional environment and geologic age show biomarkers derived from organisms that are known to have derived from biological precursor that evolved by that time. Such proofs are considered irrefutable by the pro-biogenic origin. However, although the theory seems to be solid and well correlates field observations, it does not account for some observed natural phenomenon.

- Oil has been discovered in the Earth's most ancient rocks, which were formed before any plants or animals existed on earth (Archeozoic rock formation) (Penner, 2006; Krayushkin, 1994).
- Professor Thomas Gold states in his book The Deep Hot Biosphere (Gold, 1992): “We have seen oil and gas fields refilling themselves, sometimes as fast as they were being drained, and many fields have already produced several times as much as earlier estimates predicted...”. The best example of this is Green Island in the Gulf of Mexico. When all the oil that could profitably be mined had been pumped out, the wells were closed. Twenty years later, those wells were found to contain more oil than before any had been removed (Penner, 2006).
- More and more oil is discovered and the predicted peak oil at first expected in the 1990s has still not been reached (Kenney, 2006).
- The recently discovered Tupi (The New York times, 2007) and Jupiter (BBC news, 2008) oil fields, offshore the coasts of Brazil, which comprise of unusual light oil, lay at surprisingly great depth (~5000 m below seafloor) and under an extremely thick layer of salt (up to 2000 m). Notably, these fields are the worlds biggest oil find since 2000.
- In terms of natural gas, thermal decomposition of organic matter does not generate products at equilibrium and thermal stress should not bring them to equilibrium over geologic time. Similarly, microbial production of methane represents a disequilibrium process. However, CH_4, CO and CO_2 have been observed in chemical and isotopic equilibrium in natural occurrences (Fiebig et al., 2007; 2009; Mango et al., 2009).

Whilst the Soviet Union faced ‘Iron Curtain’ isolation from the West during the Cold War in the 1950s, finding sufficient oil indigenously was a national security priority of the highest order for Russia that had little oil to fuel its economy. Scientists began a fundamental inquiry in the late 1940’s: where does oil come from? In 1956, Pr. Vladimir B. Porfir’yev stated that oil was abiogenic: “The overwhelming preponderance of geological evidence compels the conclusion that crude oil and natural petroleum gas have no intrinsic connection with biological matter originating near the surface of the Earth. They are primordial materials which have been erupted from great depths” (Porfir’yev, 1956). Similar conclusions were obtained later on (e.g. Chekaliuk 1971; Mogarovskiy et al., 1980; Chekaliuk and Kenney, 1991) and for half a century now scientists from the former Soviet Union have recognised that the petroleum is produced abiotically in the FSU fields (AAPG conference, 2004). That radically different Russian and Ukrainian scientific approach to the discovery of oil was used in the early 1990s, well after the dissolution of the USSR, to drill for oil and gas in a region believed for more than forty-five years to be geologically barren: the Dnieper-Donets Basin located between Russia and Ukraine (Krayushkin et al., 1994). A total of sixty one wells were drilled, of which thirty seven were commercially productive, an extremely impressive exploration success rate of almost sixty percent; and these Middle East fields could well produce oil forever (Mahfoud and Beck, 1995). As for the association of biomarkers with oil, the presence of microbial communities in the subsurface could account for the presence of these large organic molecules (Gold, 1992; Takai, 2004). Moreover, Kenney (1995) proposed that some of these biomarkers (e.g. pristane, phytane, porphyrin) are not necessarily of biogenic origin.

Since then the theory has reached other countries and is growing importance (e.g. Szatmari, 1989; Sugisaki and Mimura, 1995; Mahfoud, 1991; AAPG conference, 2004; Glasby, 2006). Especially when hydrothermal systems where discovered in the 1970s, methane and other lighter hydrocarbons were suggested to form abiotically in those environments (e.g. Ingmanson and Dowler, 1977; Charlou et al., 1998; 2002). A recent study by Proskurowski and coworkers (2008) strongly support the abiogenic origin of hydrocarbon gases at the Lost City hydrothermal field. Furthermore, the occurrence of chemical and isotopic equilibrium between CH_4, CO_2 and CO in natural environments, both terrestrial and marine, indicates that portion of methane may be abiogenic (Fiebig et al., 2009; Mango et al., 2009). However, the abiogenic formation of hydrocarbons has been estimated to be a minor contribution for global hydrocarbon reservoirs and the global atmospheric budget (Sherwood Lollar et al., 2002; Fiebig et al., 2009). Finally, olivine, which is the main mineral involved in the serpentinisation reaction, is not only focused in the Earth's mantle but is found in many other geological environment on earth such as sedimentary basins in the form of pebbles or serpentinites conglomerates (Beinlich et al., 2009); so that the reactions called upon in the abiotic synthesis of methane (serpentinisation + FTT) may actually be a lot more widespread on Earth than thought and increase the abiotic methane's global budget.

8 Field work

8.1 Sampling

Individual hydrothermal vent fields are first roughly located by mapping at a resolution of about 100 meters. The combination of bathymetry, bottom photography, the search for physical and chemical anomalies in the water column with sensors, and water samples, constitute a holistic approach in defining the potential active areas. Later, submarines and remotely operated vehicles (ROV) dives enable localisation of the vents and detailed study. ***(Figure 14, Figure 15)***

Figure 14: Ifremer's Remote Operated Vehicle (ROV) "Victor 6000". (http://www.ifremer.fr/flotte/systemes_sm/engins/victor.htm - © Ifremer)

Figure 15: Ifremer's manned submarine "Nautile". (MOMARDREAMnaut cruise, 2007 - © Ifremer)

Air-tight, carefully cleaned, titanium syringes are used to collect the hot fluids right at the nose of the black smokers ***(Figure 16, Figure 17)*** which minimises the risk of mixing with surrounding seawater. As soon as syringes come back to the surface, H_2S and pH measurement are carried out which enable a quality assessment of the sample, so that the purest fluid (i.e. less mixing with seawater) of each batch can be selected for immediate, on-board, gas analyses and on-board conditioning for organic studies. Aliquots of all samples are stored for inorganic chemistry analyses.

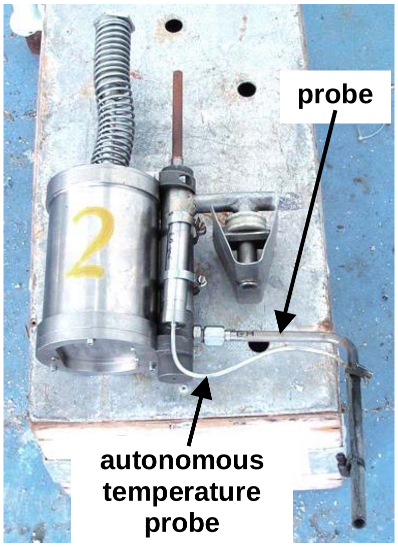


Figure 16: Titanium syringes used for hydrothermal fluids collection. (Images © Ifremer / MOMAR08-leg2)

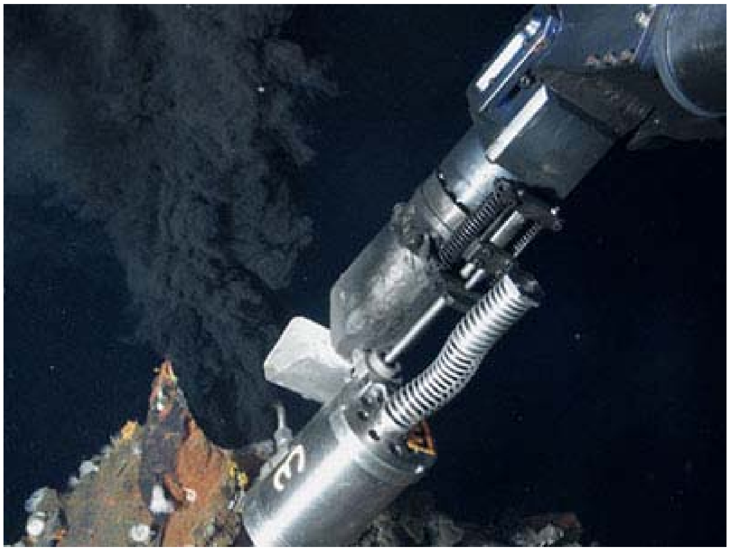


Figure 17: Sampling a black smoker. (Images © Ifremer / Serpentine 2007)

8.2 Sample preparation

For the mere reason that concentrations of organic compounds are very low in hydrothermal fluids and that salts and metals present in the latter may interfere with analytical techniques, samples must be prepared before analyses. The choice of the extraction method was based on four major criteria:

a. for a holistic approach, the method should extract a wide range of compounds
b. sample volumes are small
c. contamination sources should be minimised
d. the protocol should be as simple as possible as preparation is done on-board
e. the method should allow carbon isotopes measurements

Liquid-Liquid Extraction (LLE) and Solid Phase Extraction (SPE) are the most common extraction techniques used in the geochemistry field. LLE is usually used with large sample volumes (litres) and require large amounts of solvents that need to be evaporated therefore the method was not the most suitable for ship laboratory work. SPE is commonly chosen when dealing with small sample volumes and the wide range of sorbent phases available on the market ensures fulfilment of most requests. On the contrary the preparation is time consuming and involves many sources of contaminations. A new and innovative technique aiming at miniaturisation was launched in the 1990s: Stir Bar Sorptive Extraction (SBSE). It consists of a magnetic rod covered in a polymer phase (PDMS, which extract almost all organic compounds) to be simply stirred in 10mL of sample, dried and stored (Paper II). As such, contaminations are kept to minimum level and time is optimised. However, the current approach used in this work for carbon isotopes measurements was not compatible with SBSE. After these considerations, we chose to prepare most of our samples using the versatile SBSE method and reserved SPE only for a few samples on which carbon isotopic analyses were to be carried out. As a result, most data contained in this study come from SBSE analyses.

9 Future work

After four years of a PhD, I have peeled only the first layer of the onion and many new ideas have grown in my mind. Now that methods and analytical parameters are developed and that hydrothermally derived compounds are clearly identified, it is time to focus on specific groups of compounds in terms of quantification to give us additional clues about their origin. In that respect, further analytical development and optimisation are needed to separate these targeted compounds from the hydrothermal mixture and to improve recovery rates. The first group that should be investigated is hydrocarbons for which distribution patterns, ratios and carbon number indices could be compared to established values for petroleum and FTT reactions. Second, carboxylic acids and amino acids also should be investigated because of their particular relevance to the origin of life.

Even though individual $\delta^{13}C$ values do not allow unambiguous conclusion about the sources of organic compounds in hydrothermal fluids, stable carbon isotope measurements should be done for all compounds of interest in order to identify trends or patterns within or between different groups of compounds. For example, what is the $\delta^{13}C$ evolution with increasing carbon number? How does that compare to FTT experiments or hydrocarbons from other geological settings? What is the isotopic signature of n-alkanoic acids compared to the n-alkanes of the same chain length? Addressing these questions and pursuing parallel experiments of hydrothermal degradation of biomass may enable us to determine reaction pathways occurring in hydrothermal systems.

In terms of supporting theories of a possible origin of life in hydrothermal systems, many other smaller compounds (C_2-C_6) would be interesting to search for and quantify. Hydrogen cyanide, methanol, formate and acetate are all potential precursors for prebiotic chemistry and abiotic formation of hydrocarbons. Methane thiol has also recently been suggested as a very good way of primary carbon fixation into organic compounds within hydrothermal vents. Moreover, in terms of hydrocarbons, there is a gap in understanding the chemistry of C_6-C_8 gap needs to be filled. Nevertheless, determining their concentration, distribution, and carbon isotopic value may give us clues on their formation pathway and how these are related to both lighter and heavier hydrocarbons.

The last points that are important to consider are the adsorption of organic compounds on minerals and clays, as well as the formation of organometallic complexes with dissolved metal ions. In the first case a large amount of organic compounds may be retained on the seafloor, i.e. a portion would remain adsorbed on the mantle rocks and/or chimneys and would not dissolve in the fluids. In the second case, dissolved organometallic complexes cannot be detected using our current analytical approach that results in a possible loss of some compounds and even a lack of detection of others. In a quantitative analysis of organic compounds in hydrothermal fluids, these issues are of major importance and need to be addressed to obtain accurate in situ concentration values. Another important aspect is that the study of adsorption processes may be useful in assessing the importance of potential surface reactions in prebiotic chemistry. The study of complex formation between metals and simple organic molecules (= potential carbon and energy sources for micro-organisms) may be relevant to the question of bioavailibility of these organic molecules for the most ancient and for current living organisms.

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Paper I

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

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Origin of life

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.

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).

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

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

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

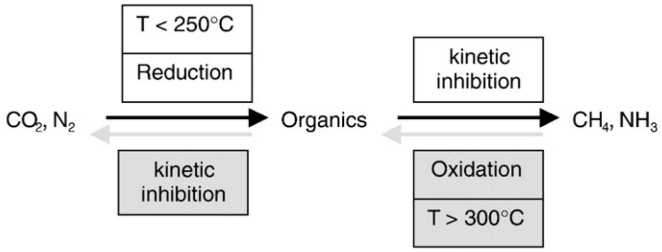

Fig. 1. Cartoon illustrating the metastable equilibrium theory among organic molecules, CO_2, N_2, CH_4 and NH_3.

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

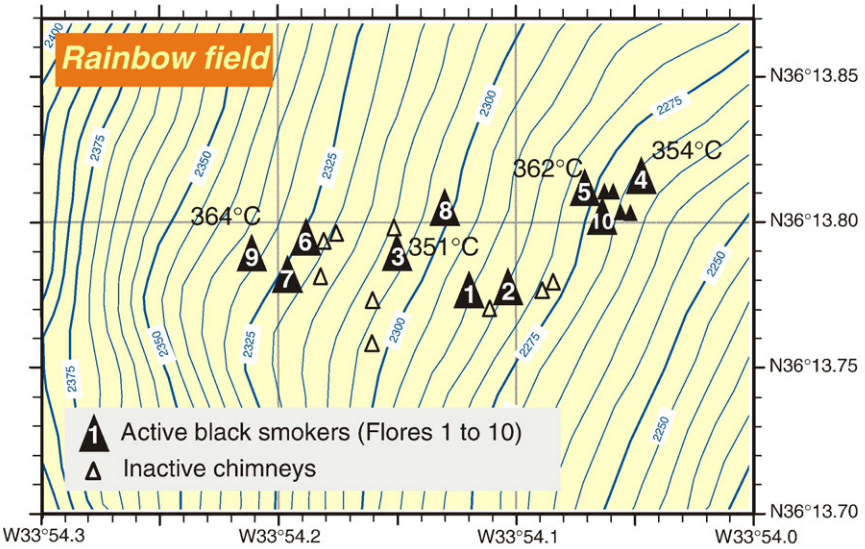

Fig. 2. Location of active black smokers at the Rainbow hydrothermal field. Even though they are spread out, the uniformity of end-member major-, minor-, trace-elements concentrations and gas contents suggests that all Rainbow fluids originate from the same de deep source. From Charlou et al. (2002), 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.

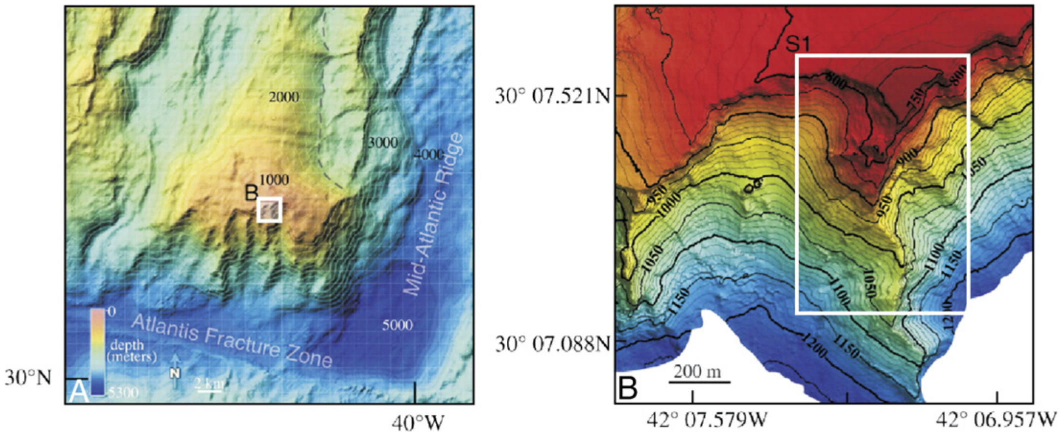

Fig. 3. A. Location map of the Atlantis Massif at 30°N along the Mid-Atlantic Ridge (MAR). The white box indicates the location of the Lost City Hydrothermal Field on the southern ridge of the massif. B. Southern wall of the Atlantis Massif. The white box shows the areal extent of the Lost City vent 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.

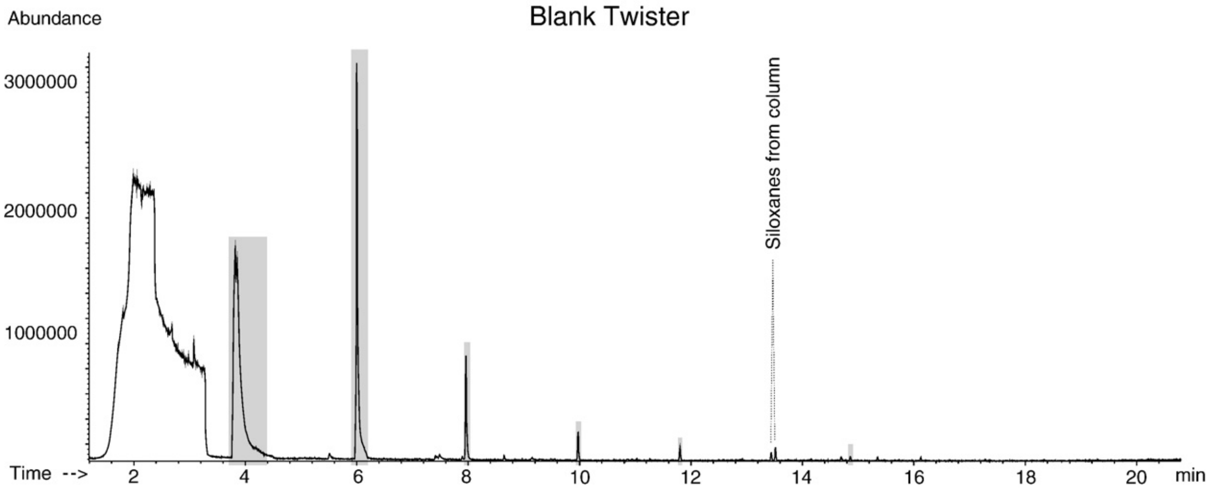

Fig. 4. GC–MS Total Ion Current (TIC) trace signature generated by a Twister after conditioning at 300 °C for 4 h under 50 mL min^{-1} purified helium flow. It consists in 6 compounds, all being siloxanes, whose retention times are 3.86, 6.00, 7.96, 9.98, 11.80, 13.44 and 14.86 min. The corresponding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

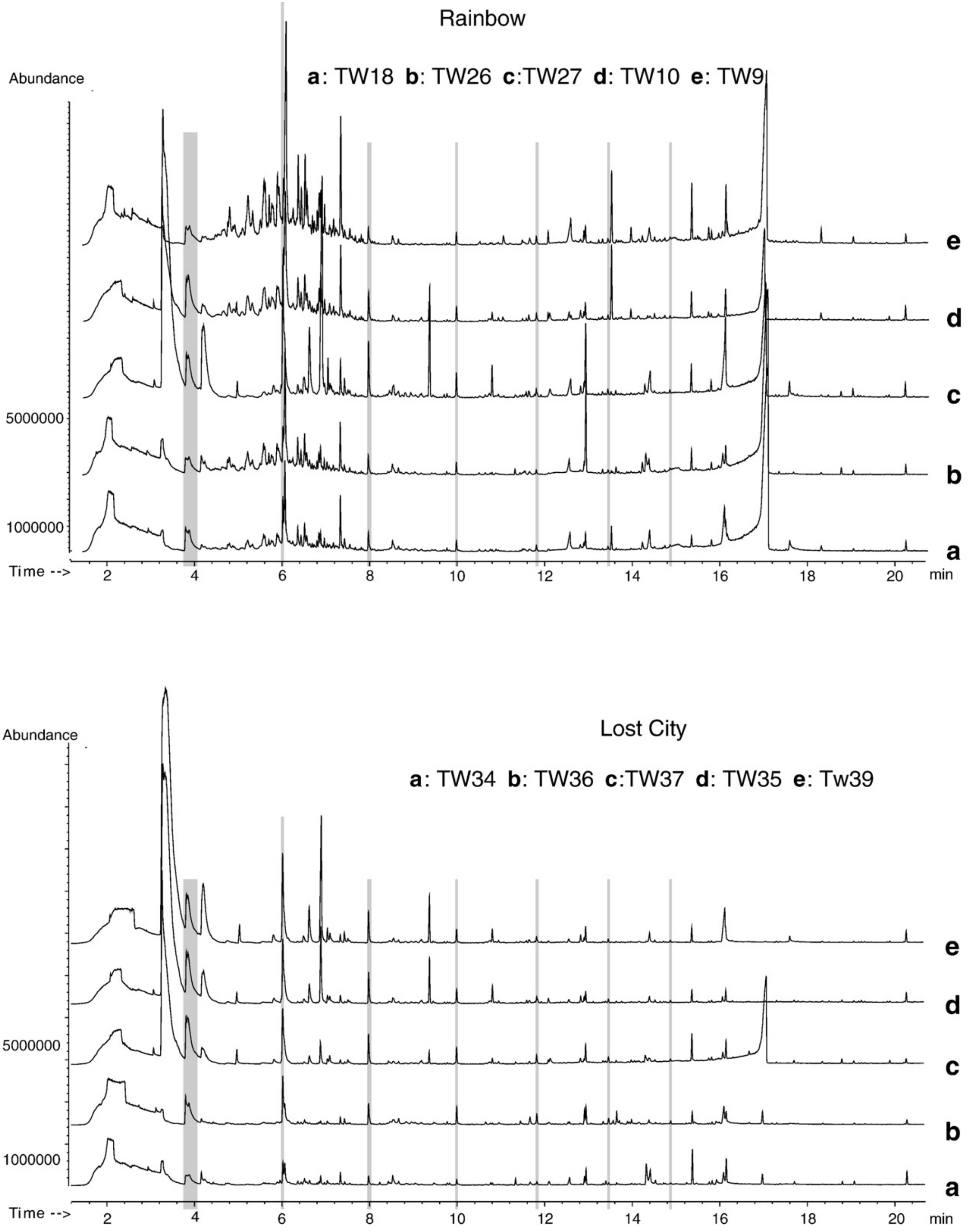

Fig. 5. Overlaid TIC chromatograms obtained after Twister extraction of 5 different samples from 5 different vents for both Rainbow (top) and Lost City (bottom) hydrothermal fields. These chromatograms revealed good consistency within one field.

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

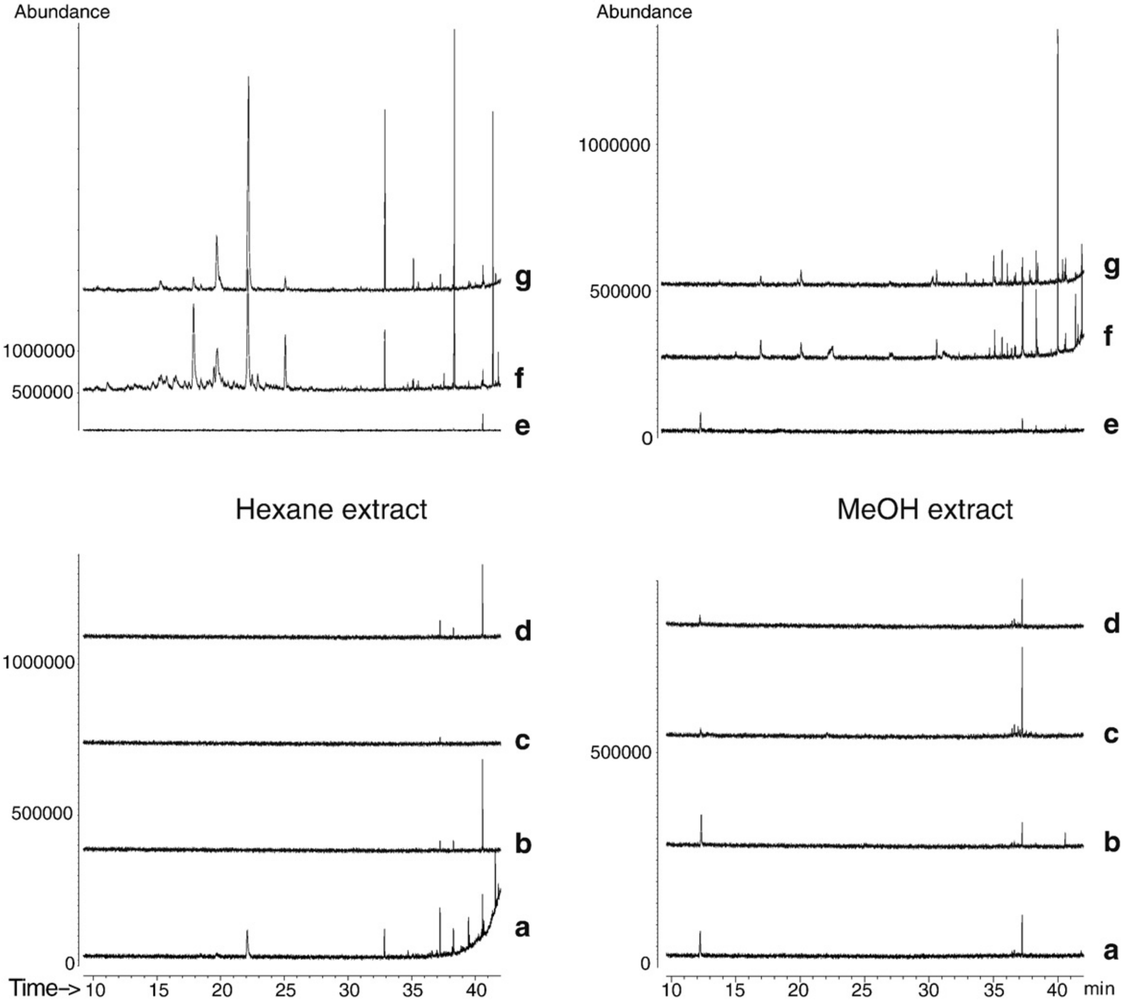

Fig. 6. Overlaid TIC Chromatograms of hydrothermal fluids extracts, deep seawater extracts and fake hydrothermal solutions extracts (a to d). TIC of hexane extracts are shown on the left and TIC of MeOH extracts on the right. a: B3, b: N1, c: A1, d: B1, e: Seawater, f: Rainbow, g: Lost City.

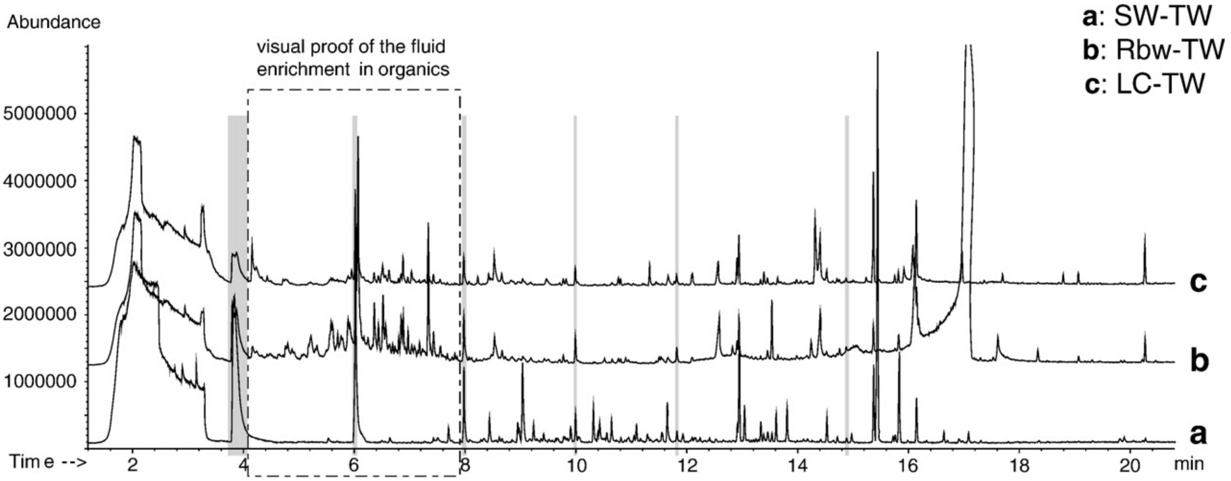

Fig. 7. GC–MS Total Ion Current (TIC) traces obtained after Twister extraction. Overlay of: a: deep seawater, b: Rainbow, c: Lost City. The 4 to 8 min zone shows the obvious enrichment in organic molecules of the Rainbow and Lost City hydrothermal fluids. In grey are the characteristic Twister's peaks.

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.

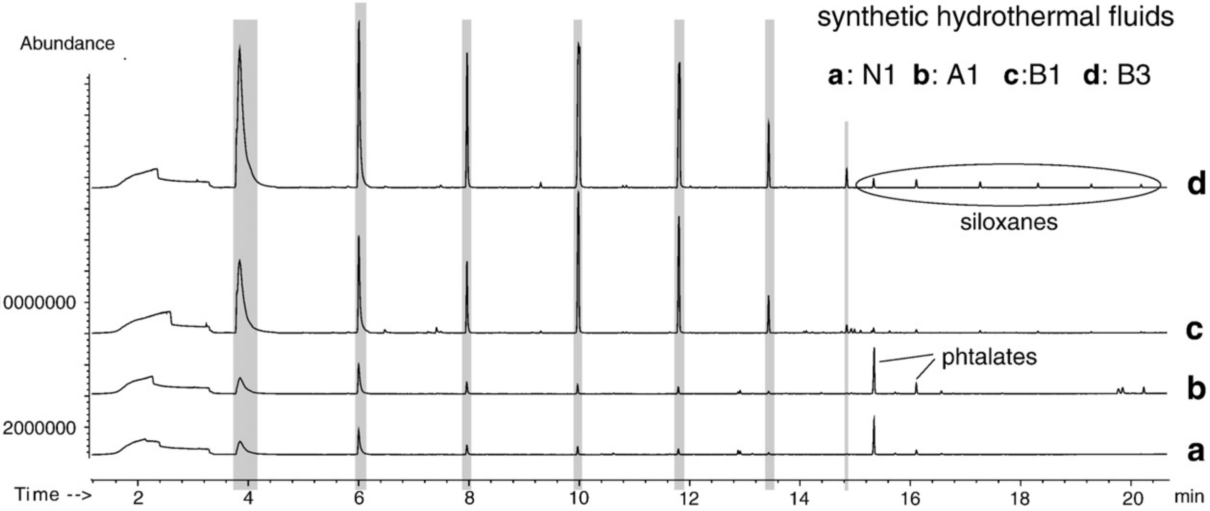

Fig. 8. Overlayed TIC Chromatograms of stir bars treated with artificial hydrothermal solutions.

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.

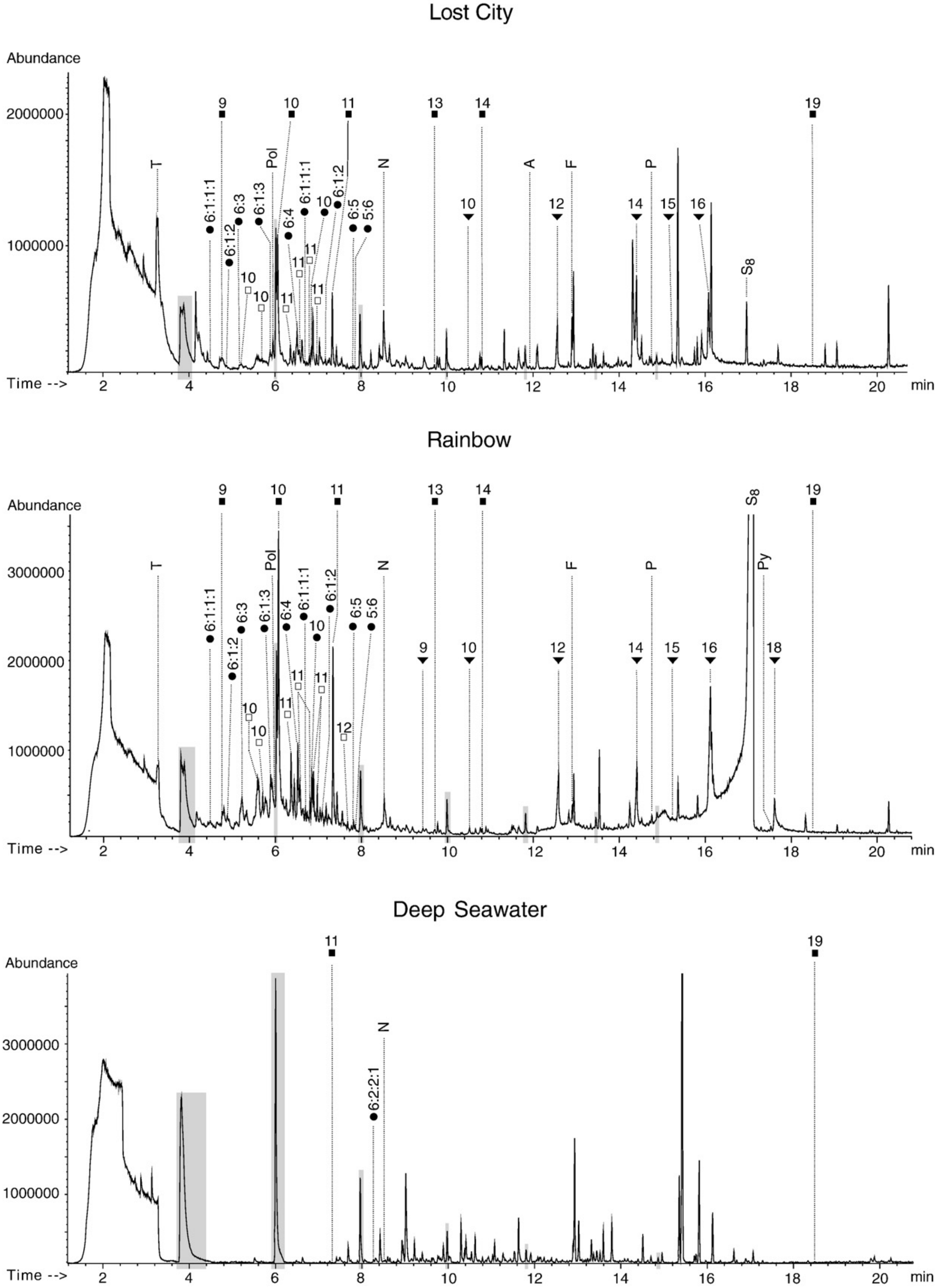

Fig. 9. GC–MS Total Ion Currents (TIC) traces of the Twister extracts for the Lost City and Rainbow fields and the deep seawater reference. Numbers stand for the total number of carbon for n-alkanes (full squares), branched alkanes (empty squares) and carboxylic acids (full triangles). Cycloalkanes (full 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	$\delta^{13}C$ (‰)	
		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 $\delta^{13}C$ 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 $\delta^{13}C$ value in the −46 to −20‰ range (Table 4). The variation of $\delta^{13}C$ 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 $\delta^{13}C$ 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 coworkers. 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

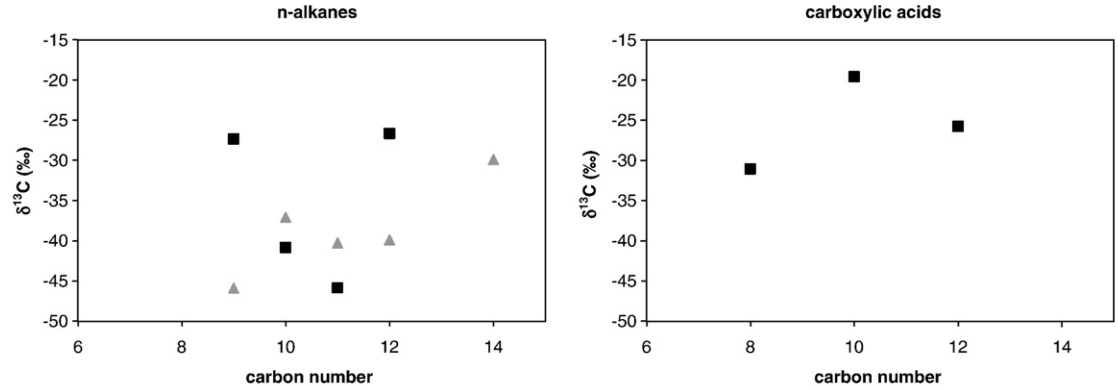

Fig. 10. Isotopic composition vs. carbon number of n-alkanes (left) and carboxylic acids (right) recorded in Rainbow (triangles) and Lost City (squares) hydrothermal fluids. Carboxylic acids in Rainbow fluids showed a signal too weak for reliable $\delta^{13}C$ measurements.

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).

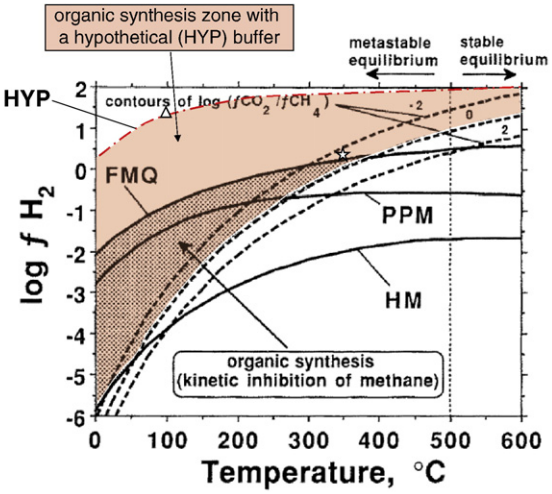

Fig. 11. Modified after Shock (1990). Plot of log fH_2 against temperature. Solid curves show values of log fH_2 buffered by the FMQ, PPM and HM mineral assemblages as functions of temperature. Dashed curves correspond to contours of $\log(fCO_2/fCH_4)$ equal to 2, 0 and −2 as function of temperature. 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.

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).

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.

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.

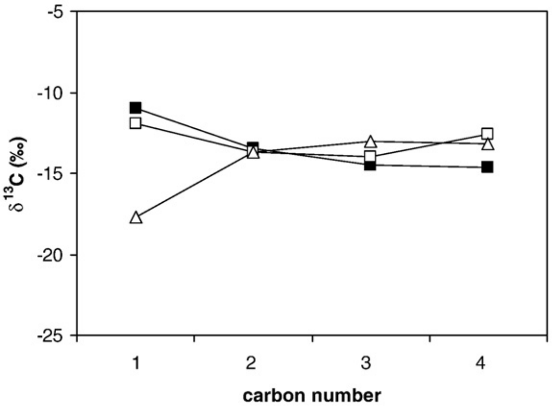

Fig. 12. Plot of δ13C values of n-alkanes against carbon number. No isomeric distinction was done for butane. Squares refer to the Lost City data; full for Proskurowski et al. (2008) and empty for this study (EXOMAR cruise 2005). Triangles refer to the Rainbow data.

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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Paper II

Detection of trace organic compounds by Stir Bar Sorptive Extraction: application to the evolution of the organic composition of hydrothermal fluids from the Rainbow site (36°N, Mid-Atlantic Ridge) over 3 years.

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Abstract

The question of the abiogenic oil has been discussed and hydrothermal reactions have been suggested to abiotically generate hydrocarbons. Besides, ultramafic-hosted hydrothermal systems have been regarded as favourable environment for the emergence of life. Therefore, it is of great importance to investigate the presence of organic compounds in hydrothermal fluids. However, because of the sampling difficulties, the complexity of the matrix, the numerous interferences and the assumed trace level concentrations; it was considered a real challenge. Here we show that Stir Bar Sorptive Extraction (SBSE) coupled to Thermal Desorption – Gas Chromatography – Mass Spectrometry (TD-GC-MS) can be successfully applied to analyses of volatile and semi-volatile organic compounds in hydrothermal fluids. The method exhibited excellent reproducibility and conditioned samples appeared to be really stable for up to 3 years. This innovative and versatile technique was used to study the fluids from the ultramafic-hosted hydrothermal field Rainbow located at 36°14’N on the Mid-Atlantic Ridge (MAR). Despite relative stability for mineral composition and gas content is observed, analyses of fluids samples from 2005, 2007 and 2008 revealed more distinct organic compositions. In addition, results suggest the similarity of the organic content of the fluids regardless of the sampling location within the field, which may indicates the presence of a single reaction zone and that no further chemical reactions occur while fluids are transported to the seafloor.

Paper III

NEW INSIGHT ON THE ORIGIN OF ORGANIC COMPOUNDS IN FLUIDS FROM ULTRAMAFIC-HOSTED HYDROTHERMAL SYSTEMS

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ABSTRACT

Hydrocarbons gases (C_1-C_4) as well as larger organic compounds were reported elsewhere in fluids from the Rainbow and the Lost City ultramafic-hosted hydrothermal fields. Whereas hydrocarbon gases are likely abiogenic (Fischer-Tropsch Type reaction), the origin of larger molecules remains unclear. Our ability to differentiate between biotic and abiotic sources of organic compounds in deep-sea hydrothermal systems may give clues to the understanding of organic geochemistry on the early Earth. Here, we report a series of experiments of hydrothermal degradation (40 MPa / 200, 350 and 450°C) of the piezophile archaea *Pyrococcus abyssi* biomass, which provides supporting lines of evidence of the abiogenic origin of saturated hydrocarbons as well as of the possible biogenic origin of alkylated aromatic hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAH) and $C_{12:0}$-$C_{16:0}$ fatty acids in fluids from ultramafic-hosted hydrothermal systems.

Paper IV

Detection of trace concentrations of amino acid in aqueous solutions by Ion-pairing reversed-phase UPLC-ESI-QToF-MS: application to hydrothermal fluids.

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Abstract

Amino acids are the fundamental building blocks of proteins that are required for the initiation of living organism, therefore they are key compounds in the origin of life quest. The abiotic production of amino acids within ultramafic-hosted hydrothermal systems was suggested a few decades ago and is strongly supported by thermodynamic data and experimental work. However, field data were clearly lacking and thus investigation of amino acids in fluids from ultramafic-hosted hydrothermal systems was of major importance. Even though amino acids analysis have been carried out routinely for several decades in various field of application, none of the currently available methods appeared suitable for our purpose because of the complexity of the hydrothermal fluids matrix (salts, minerals, gases) and the extremely low concentrations of amino acids that were expected. We took up the challenge and here we describe a method to detect underivatized amino acids down to the sub-ppb level in aqueous matrix by ion-pairing reverse-phase Ultra-high Performance Liquid Chromatography - Electrospray Ionisation - Quadrupole Time of Flight - Mass Spectrometry (UPLC-ESI-QTOF-MS). Characterisation and separation of 10 chosen proteinogenic amino acids was achieved and excellent linearity in the response was obtained for all amino acids with correlation coefficient > 0.9921. This analytical method was successfully applied to natural hydrothermal fluid samples from ultramafic-hosted vents of the Mid-Atlantic Ridge region. Tryptophan and Phenylalanine were clearly evidenced in the fluids and concentrations of Leucine reached 15-55 ppt. We suggest that other amino acids are present in hydrothermal fluids but occur for the major part as metal and/or clay complexes and could not be detected using current approach. Finally, concentrations of amino acids measured in the deep seawater reference sample were in good agreement with generally accepted background level in the deep ocean.

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