

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

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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 Magnér. I was lead author on all papers and did data interpretation as well as the writing.

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 (CH₄) from carbon dioxide (CO₂) and hydrogen (H₂) 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. CH₄) 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 croûte 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 définit 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'anciens 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 $>400^{\circ}\text{C}$. 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 événements 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.



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. CO₂). 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 MnO₂ 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).

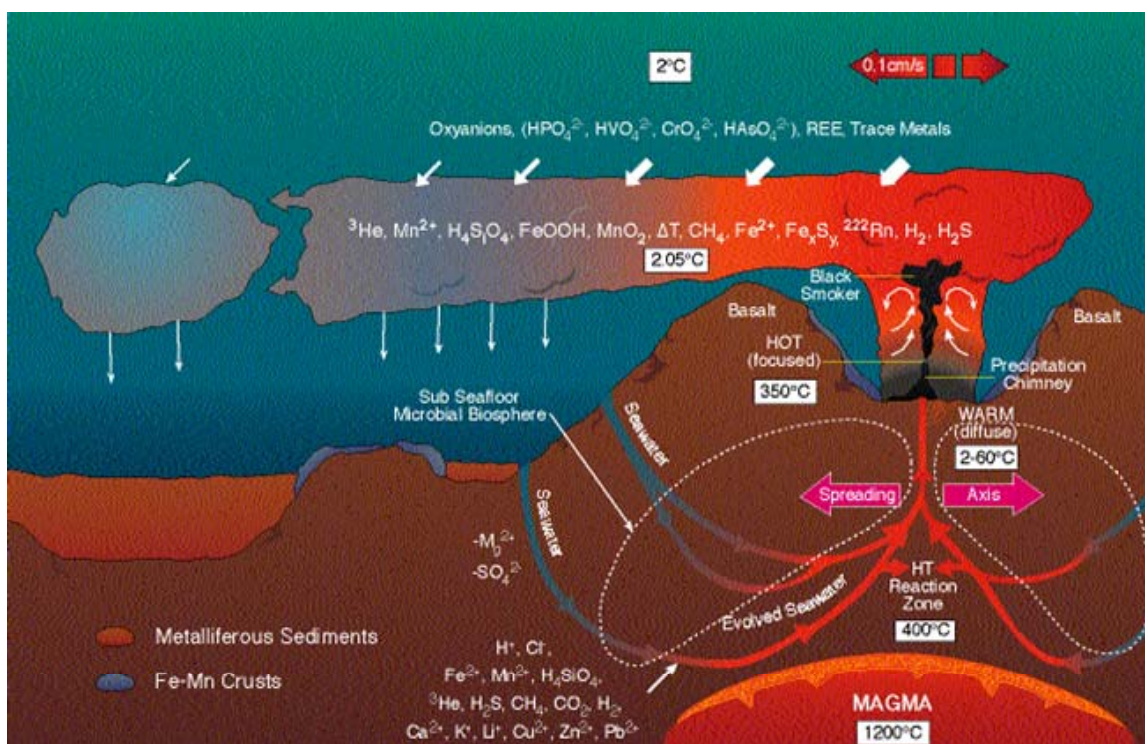


Figure 1: cartoon illustrating the hydrothermal circulation and the evolution of the fluid composition during its journey in the subsurface. (From NOAA website)

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.

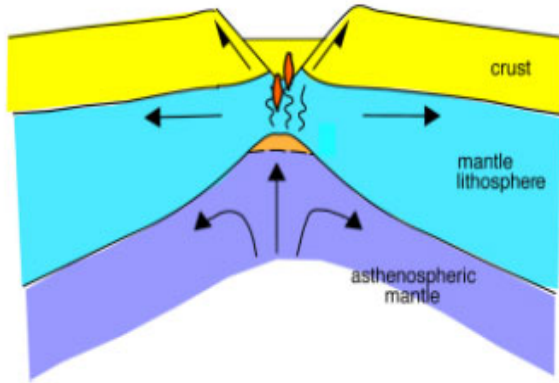
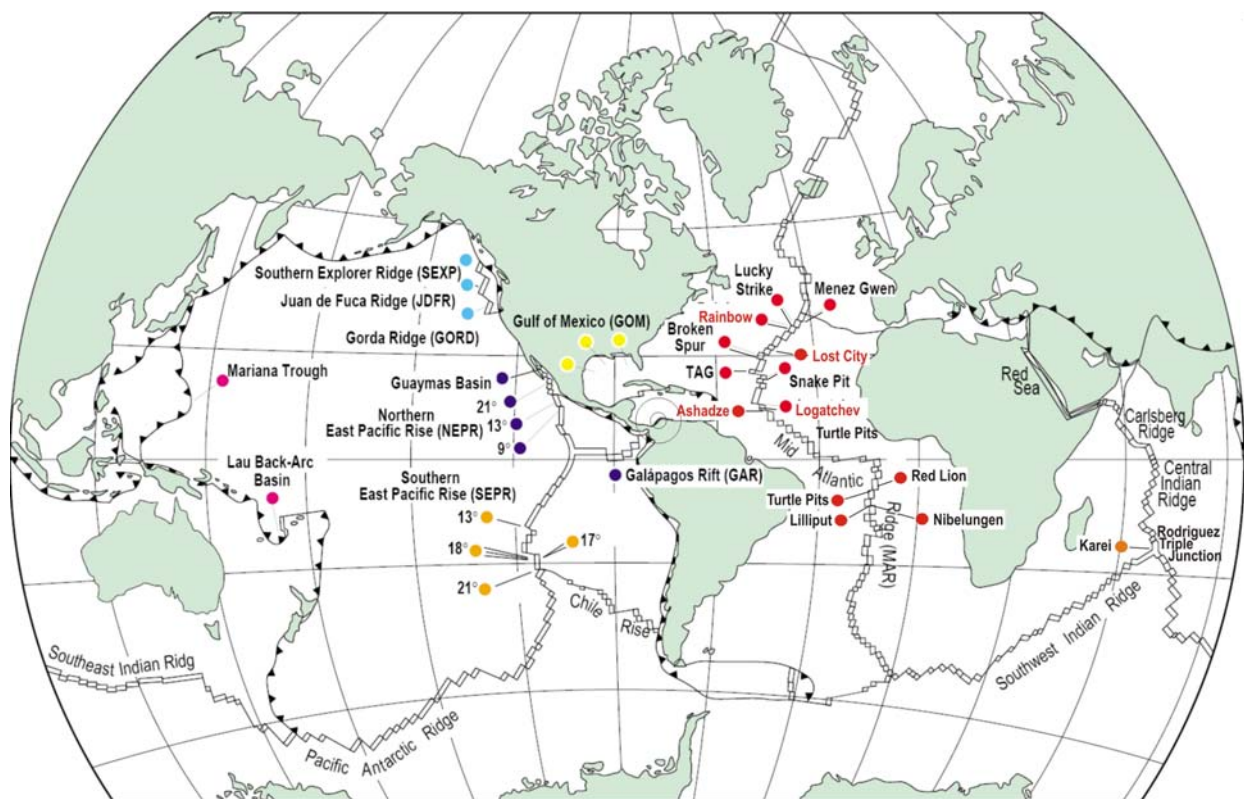


Figure 2: Schematic view of a slow spreading ridge showing the large extensional faults that form the walls of the axial valley and bring up the most superficial levels of the mantle. These superficial levels are called lithospheric mantle because the peridotites are relatively cold (less than 1000 °C) 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.



The mid-ocean ridge system and associated hydrothermal vents and hydrocarbon seeps

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.

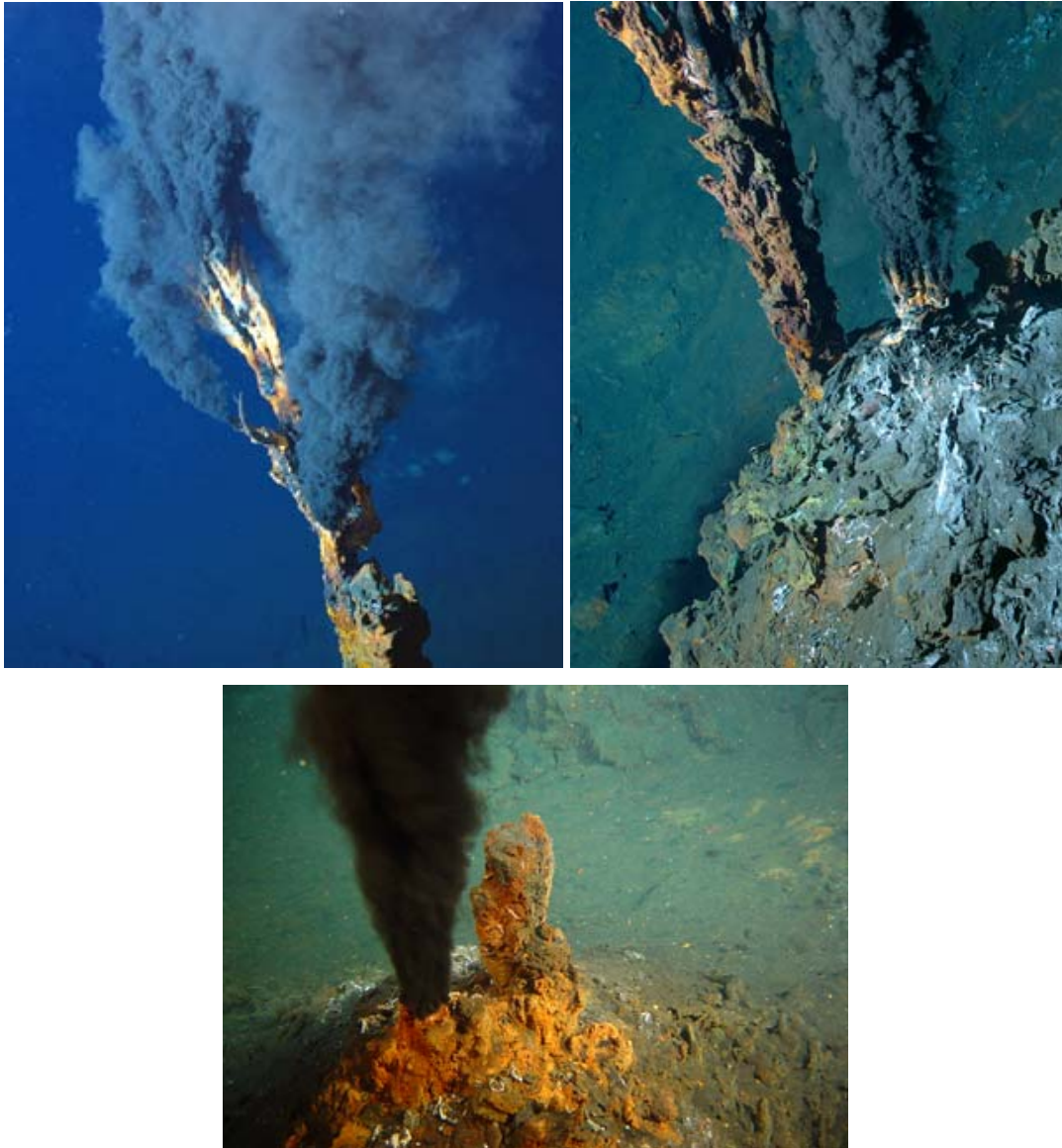


Figure 4: Black smokers at the Rainbow hydrothermal field. Images © Ifremer / MoMARDREAMnaut 2007 and MOMAR08-Leg2 2008 cruises.

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 H₂ and CH₄ are observed. The only serpentinisation equilibria dominating here result in low-temperature (<90°C) and alkaline (pH=10-11) fluids as well as low CO₂ 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, CO₂, CH₄, H₂, H₂S 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).

	<i>Location</i>	<i>pH</i>	<i>T (°C)</i>	<i>Depth (m)</i>	<i>Cl</i>	<i>CO₂</i>	<i>CH₄</i>	<i>H₂</i>	<i>H₂S</i>
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. Various 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).

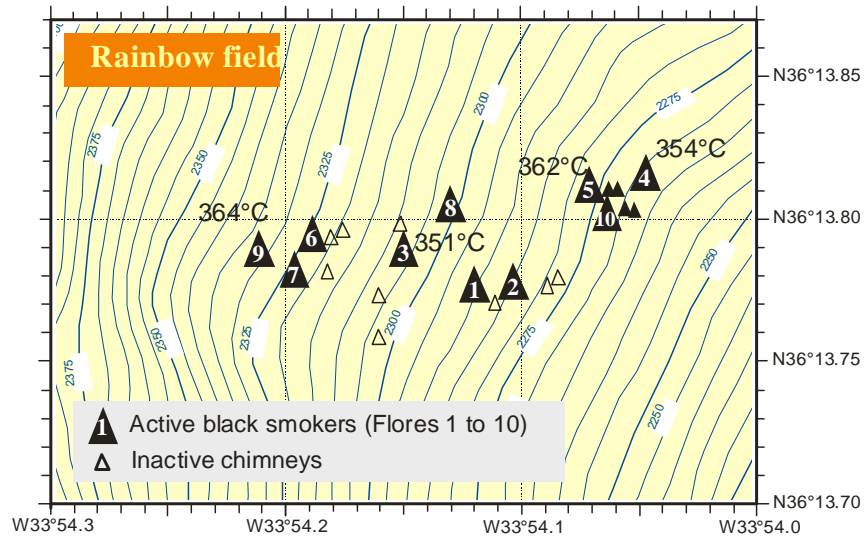


Figure 6: Location of active black smokers at the Rainbow hydrothermal field (From Charlou et al., 2002). This map was established during the FLORES 1997 cruise but the smokers were resampled during the EXOMAR 2005, MoMARDREAMnaut 2007 and MOMAR08 - Leg 2 2008 cruises all conducted by Ifremer. Full triangles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

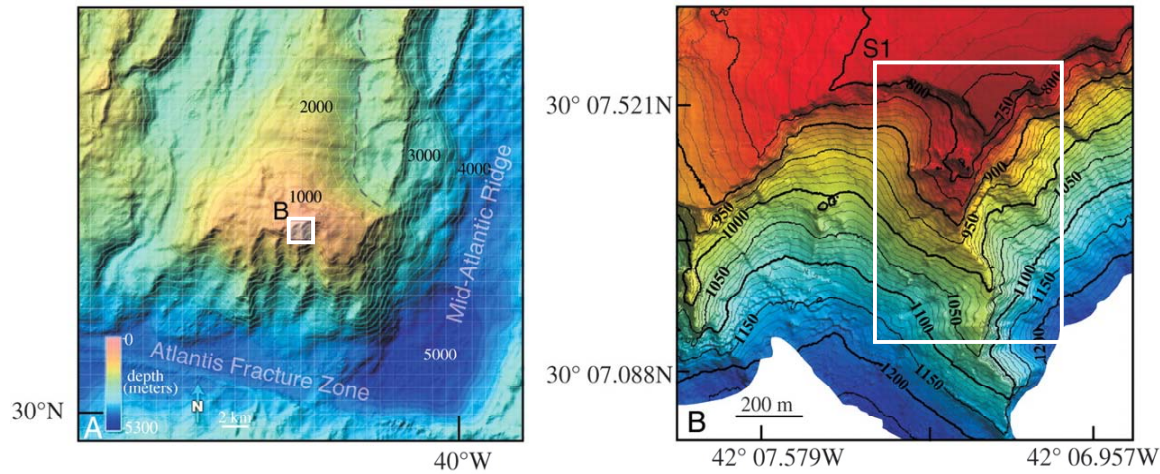


Figure 7: A. Location map of the Atlantis Massif at 30°N along the Mid-Atlantic Ridge (MAR). The white box indicates the location of the Lost City Hydrothermal Field on the southern ridge of the massif. B. Southern wall of the Atlantis Massif. The white box shows the areal extent of the Lost City vent 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°50'W 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.

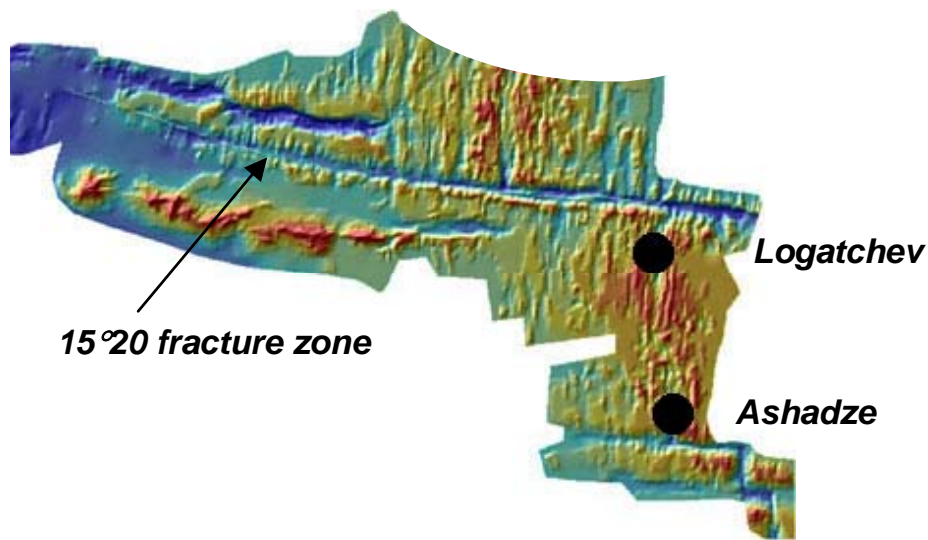


Figure 8: Location of the Logatchev and Ashadze hydrothermal field south of the 15°20' fracture zone, on the MAR axis. (Modified after H el ene Ondreas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Serpentine cruise, 2007, Ifremer)

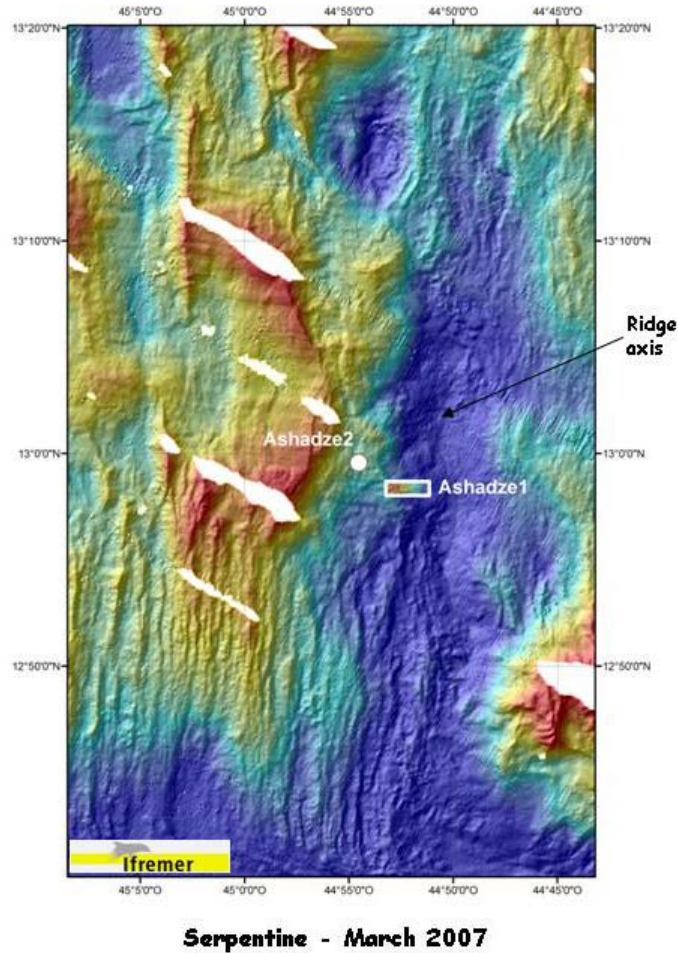


Figure 9: Detailed bathymetric map around the Ashadze hydrothermal field and location of the sites Ashadze1 and Ashadze 2. (Modified after H el ene Ondr eas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Serpentine cruise, 2007, Ifremer)

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).

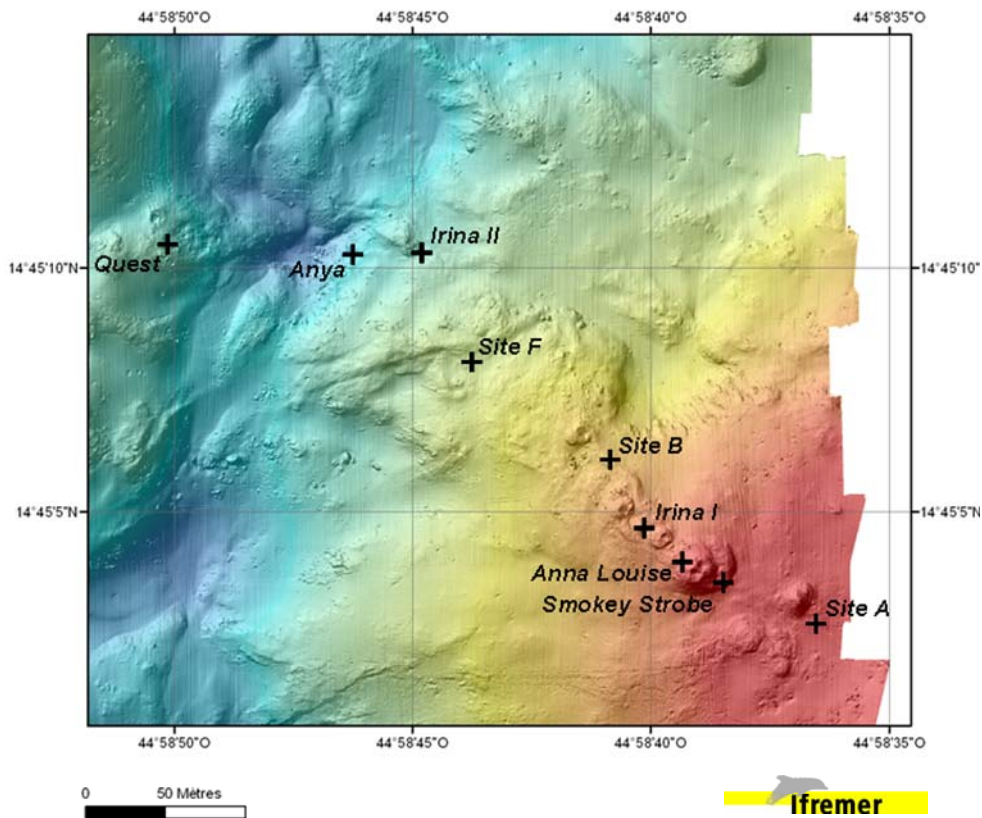


Figure 10: Detailed bathymetric map of the Logatchev 1 site and location of the active vents. (Modified after H el ene Ondr eas, Ifremer – from data acquired by the MMR on the ROV Victor6000 - Dive 315 - Serpentine cruise, 2007, Ifremer)

4 H₂ generation during serpentinisation

Serpentinised ultramafic rocks have received considerable attention as a source of H₂ 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 CO₂ or CO by H₂ 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 H₂ 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 H₂ 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 (Fe₃O₄) while hydrogen from water is reduced to H₂. 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 H₂ 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 H₂. 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 H₂ 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, H₂ 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 than magnetite, explaining the decrease in H₂ concentrations. At temperatures above 315°C, olivine becomes stable and the generation of H₂ 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, H₂ is still produced via alteration of pyroxenes. (*Figure 11*)

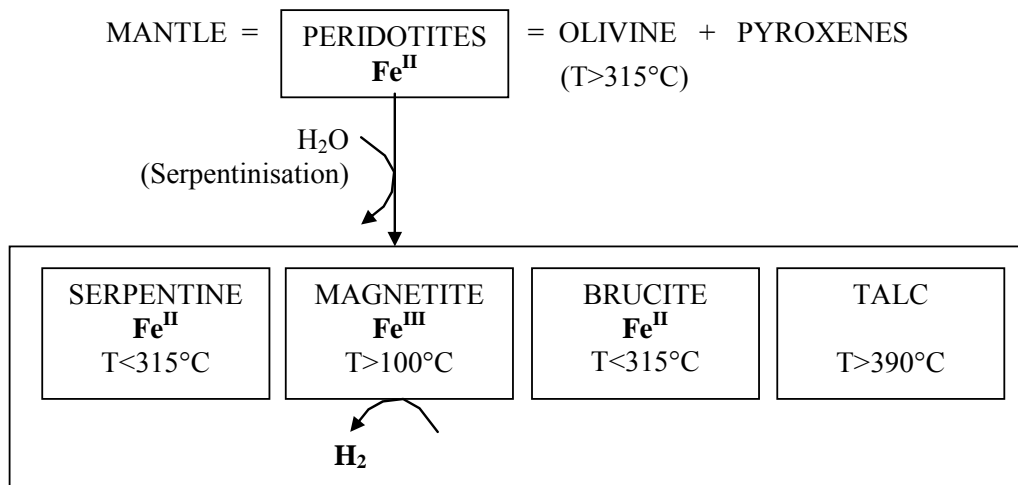


Figure 11: Schematic of the serpentinisation reaction. It produces different minerals depending on the temperature. For each mineral the temperature above or under which it is stable is given. The schematic highlights the fact that only the conversion of Fe^{II} to Fe^{III} produces H₂.

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 H₂ will always be higher at low W:R than at high W:R despite a higher production of H₂ per kg of rock (diluted in more water). Even at high W:R the concentrations of H₂ 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 H₂ production is higher. At 350°C, the variation in

the H₂ 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 H₂ at 300°C and very low W:R, however such concentrations cannot be reached because they exceed the solubility of H₂ and the accumulation of H₂ is limited in any case by the formation of native metals, particularly Fe-bearing alloys. As a result, the authors concluded that H₂ 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 H₂ during serpentinisation. Particularly at low temperatures kinetic factors would further limit rates of H₂ production. At temperatures $>\sim 200^{\circ}\text{C}$ 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 H₂ production.

4.4 Implications for H₂-based microbial communities and abiotic synthesis

In environments with temperatures low enough to sustain microbial communities ($<120^{\circ}\text{C}$), the model indicates that partitioning of Fe into brucite may significantly restrict the amount of H₂ 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 H₂ concentration to lower values than field measurements. According to the model, to explain the concentration of H₂ 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 H₂ 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 H₂ according to the model of McCollom and Bach (2009). Serpentinisation may definitely be the sole process responsible for the entire production of H₂ in ultramafic-hosted hydrothermal systems considering that the model of McCollom and Bach (2009) predicts concentrations of H₂, 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 H₂ 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 H₂ with CO₂, which would be favourable under high H₂ concentrations. According to the model predictions, ultramafic rocks undergoing alteration in the 200-315°C should generate the greatest amounts of H₂ 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 assess 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 H₂ and CH₄, high H₂S and silica concentration and enrichment in Light Rare Earth Elements (LREE) as well

as magmatic volatiles such as CO₂ (Douville et al., 2002). Whereas, high concentrations of reduced gases (H₂ and CH₄), low H₂S 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 ($T_c = 407\text{ °C}$, $P_c = 298\text{ bar}$), 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

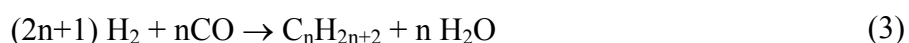
understood; and neither are the processes controlling the organic chemistry of the fluids. Both the sources of the building units composing organic molecules (C, H, O and N) and possible reaction pathways leading to organic compounds are multiple, therefore determining the origin of organic compounds 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, CO₂ and carbonates for C, H₂ and water for H, N₂ and NH₃ 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, CH₄, H₂, acetate, CO₂), (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 CH₄ 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 CO₂/CH₄ and N₂/NH₃ 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 CO₂ 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:



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 H₂ 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 (CH₄).

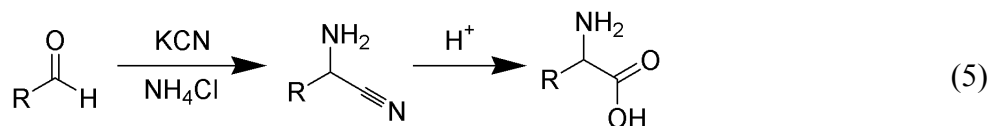
Carbon sources other than CO can be utilized and the reaction will still occur. In hydrothermal systems, CO₂ is the most likely reactant and numerous laboratory experiments (McCollom et al., 1999; McCollom and Simoneit, 1999; McCollom, 2000; Rushdi and Simoneit, 2001, 2004, 2005, 2006; Seewald et al., 2006) have shown that saturated hydrocarbons as well as other organic compounds can be abiotically produced via FTT reactions under hydrothermal conditions, with CO₂ 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 CO₂ by H₂ (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):



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 CO₂) and nitrogen (N₂) 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

Chemolithotroph microbial communities commonly colonize hydrothermal vents and may represent analogs for life on the early Earth and other planets. Chemolithotrophic 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 CH₄ from CO₂

and H₂. 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 CO₂. Also from CO₂ and H₂, 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.

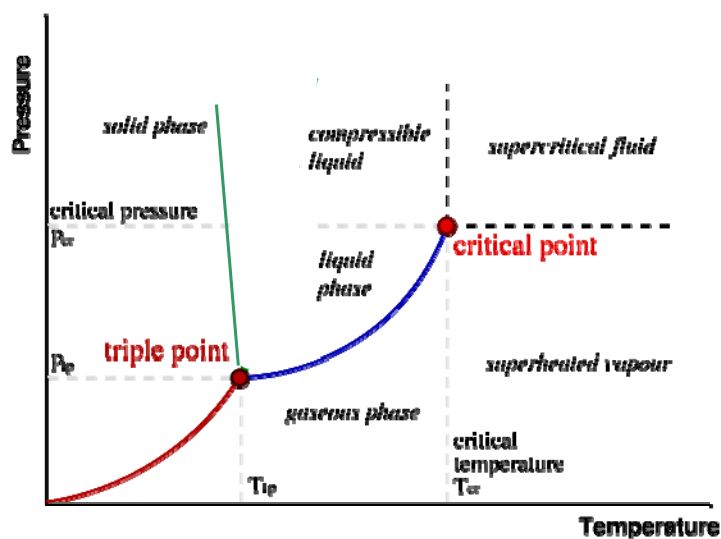


Figure 12: Phase diagram of water. Modified after <http://en.wikipedia.org/wiki/File:Phase-diag2.svg>.

Conditions near and above the seawater critical point ($T_c = 407\text{ }^\circ\text{C}$, $P_c = 29.8\text{ MPa}$) 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.

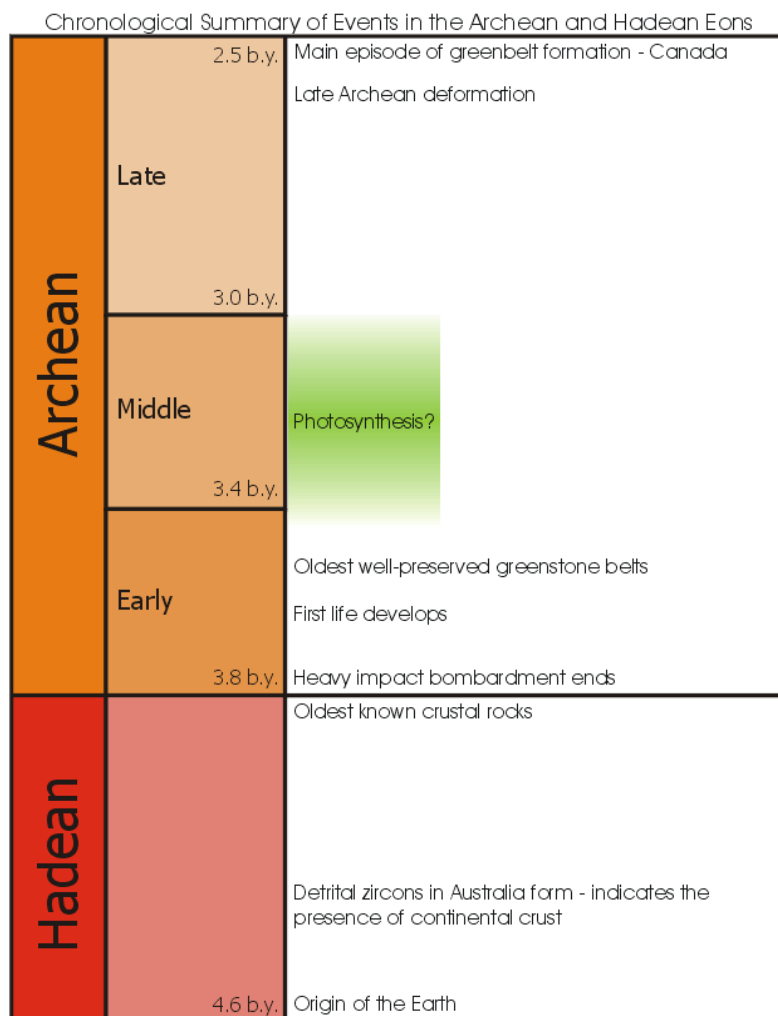


Figure 13: History column and major events in the Hadean - Archean Eons. To be noted the date of apparition of photosynthesis is subject to current debate (Allwood et al., 2009). From Winona State University website <http://www.winona.edu/geology/MRW/mrwimages/ArcheanHistoryColumn.gif>

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 CO₂, N₂, H₂O and little amount of H₂S with CO₂ 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, SO₂ and elemental sulphur S⁰ and minor amounts of H₂ and Ar (Russell and Arndt, 2005). Finally, different lines of evidences indicate the presence of CH₄ 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 CH₄ 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 N₂ 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 CO₂ appears difficult to estimate on early Earth, however CO₂ was definitely present in the ocean via dissolution of atmospheric CO₂ (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). Mg²⁺ together with Ca²⁺ 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 CH₄ or H₂O 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; Eglinton 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, CH₄, CO and CO₂ 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 were 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 CH₄, CO₂ 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, H₂S 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.

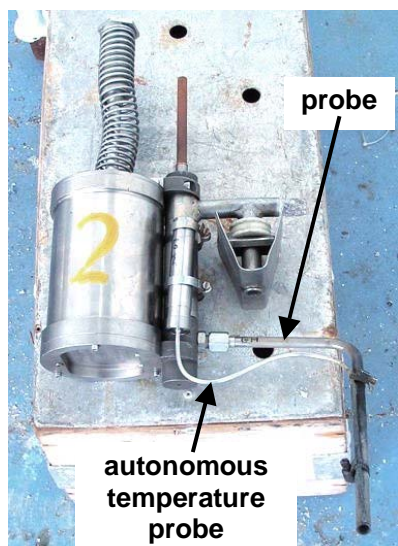


Figure 16: Titanium syringes used for hydrothermal fluids collection. (Images © Ifremer / MOMAR08-leg2)



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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 ($\text{C}_2\text{-C}_6$) 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 $\text{C}_6\text{-C}_8$ 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 bioavailability of these organic molecules for the most ancient and for current living organisms.

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11 References

- AAPG Hedberg Research Conference (2004) *Origin of Petroleum: Biogenic and/or Abiogenic and its Significance to Hydrocarbon Exploration and Production, July 11-14, Vienna, Austria*, <http://www.mail-archive.com/ctrl@listserv.aol.com/msg111373.html>
- Abelson, P.H. (1966) Chemical Events on the Primitive Earth. *Proceedings of the National Academy of Sciences of the United States of America*, **55**(6): 1365-1372.
- Akiya, N. and Savage, P.E. (2002) Roles of Water for Chemical Reactions in High-Temperature Water. *Chemical Reviews*, **102**(8): 2725-2750.
- Albrecht, P. and Ourisson, G. (1971) Biogenic substances in sediments and fossils. *Angewandte Chemie International Edition*, **10**: 209-225.
- Allen, D.E. and Seyfried, W.E. (2004) Serpentinization and heat generation: constraints from Lost City and Rainbow hydrothermal systems. *Geochimica et Cosmochimica Acta*, **68**(6): 1347.
- Allen, D.E. and Seyfried, W.E. (2003) Compositional controls on vent fluids from ultramafic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500 bars. *Geochimica et Cosmochimica Acta*, **67**(8): 1531-1542.
- Allwood, A.C., Grotzinger, J.P., Knoll, A.H., Burch, I.W., Anderson, M.S., Coleman, M.L. and Kanik, I. (2009) Controls on development and diversity of Early Archean stromatolites. *Proceedings of the National Academy of Sciences of the United States of America*, **106**(24): 9548-9555.
- Alt, J.C. and Shanks, W.C.I. (1998) Sulfur in serpentinized oceanic peridotites: Serpentinization processes and microbial sulfate reduction. *Journal of Geophysical Research*, **103**(B5): 9917-9930.
- Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W., Scott, C., Garvin, J. and Buick, R. (2007) A Whiff of Oxygen Before the Great Oxidation Event? *Science*, **317**(5846): 1903-1906.
- Askhabov, A. (2008) The quateron hypothesis of the origin of life. *Doklady Biological Sciences*, **418**(1): 50-52.

- Augustin, N., Lackschewitz, K.S., Kuhn, T. and Devey, C.W. (2008) Mineralogical and chemical mass changes in mafic and ultramafic rocks from the Logatchev hydrothermal field (MAR 15°N). *Marine Geology*, **256**(1-4): 18-29.
- Batuev, B.N., Krotov, A.G., Markov, V.F., Cherkashev, G.A., Krasnov, S.G. and Lisitzin, Y.D. (1994) Massive sulfide deposits discovered at 14°N45', Mid-Atlantic Ridge. *BRIDGE Newsletter*, **6**: 6-10.
- BBC news (2008) 'Huge' gas field found off Brazil, **Tuesday, 22 January**.
- Beinlich, A., Austrheim, H., Glodny, J., Erambert, M. and Andersen, T.B., 2009. CO₂ sequestration and extreme Mg leaching in serpentinized peridotites clasts of the Devonian Solund Basins, SW-Norway, *Goldschmidt Conference, Davos, Switzerland*.
- Beltenev, V., Ivanov, V., Shagin, A., Segeyev, M., Rozhdestvenskaya, I., Shilov, V., Debretsova, I., Cherkashev, G., Samovarov, M. and Poroshina, I. (2005) New hydrothermal sites at 13°N, Mid-Atlantic Ridge. *InterRidge News*, **14**: 14-16.
- Beltenev, V., Nescheretov, A., Shilov, V., Ivanov, V., Shagin, A., Stepanova, T.V., Cherkashev, G.A., Batuev, B., Samorarov, M., Rozhdestvenskaya, I., Andreeva, I., Fedorov, I., Davidov, L., Romanova, A., Rummyantsev, A., Zaharov, V., Luneva, N. and Artemeva, O. (2003) New discoveries at 12°58'N, 44°52'W, MAR: Professor Logatchev-22 cruise, initial results. *InterRidge News*, **12**: 13-14.
- Berndt, M.E., Allen, D.E. and Seyfried, W.E., Jr. (1996) Reduction of CO₂ during serpentinization of olivine at 300°C and 500 bar. *Geology*, **24**(4): 351-354.
- Bischoff, J.L. and Rosenbauer, R.J. (1987) Phase separation in seafloor geothermal systems; an experimental study of the effects on metal transport. *American Journal of Science*, **287**(10): 953-978.
- Boetius, A. (2005) OCEAN SCIENCE: Lost City Life. *Science*, **307**(5714): 1420-1422.
- Bougault, H., Aballea, M., Radford-Knoery, J., Charlou, J.L., Baptiste, P.J., Appriou, P., Needham, H.D., German, C. and Miranda, M. (1998) FAMOUS and AMAR segments on the Mid-Atlantic Ridge: ubiquitous hydrothermal Mn, CH₄, δ³He signals along the rift valley walls and rift offsets. *Earth and Planetary Science Letters*, **161**(1-4): 1.
- Brandes, J.A., Boctor, N.Z., Cody, G.D., Cooper, B.A., Hazen, R.M. and Yoder, H.S., Jr. (1998) Abiotic nitrogen reduction on the early Earth. *Nature*, **395**(6700): 365.
- Campbell, A.C., Palmer, M.R., Klinkhammer, G.P., Bowers, T.S., Edmond, J.M., Lawrence, J.R., Casey, J.F., Thompson, G., Humphris, S., Rona, P. and Karson, J.A. (1988) Chemistry of hot springs on the Mid-Atlantic Ridge. *Nature*, **335**(6190): 514-519.
- Cannat, M. (1993) Emplacement of Mantle Rocks in the Seafloor at Mid-Ocean Ridges. *Journal of Geophysical Research*, **98**.
- Cannat, M., Lagabrielle, Y., Bougault, H., Casey, J., de Coutures, N., Dmitriev, L. and Fouquet, Y. (1997) Ultramafic and gabbroic exposures at the Mid-Atlantic Ridge: geological mapping in the 15°N region. *Tectonophysics*, **279**(1-4): 193-213.
- Cannat, M., Ondreas, H., Fouquet, Y., Silantiev, S., Hoisé, E., Fontaine, F. and Scientific Party, S. (2007) Geological Context of Ultramafic-Hosted Hydrothermal Vent Fields in the 13-15°N Region of the Mid Atlantic Ridge : Preliminary Results of the Serpentine Cruise. *Eos, Transactions, American Geophysical Union*, **88**(52): T51F-02.
- Charlou, J.L., Donval, J.P., Douville, E., Jean-Baptiste, P., Radford-Knoery, J., Fouquet, Y., Dapoigny, A. and Stievenard, M. (2000) Compared geochemical signatures and the evolution of Menez Gwen (37 Deg50'N) and Lucky Strike (37 Deg17'N) hydrothermal fluids, south of the Azores Triple Junction on the Mid-Atlantic Ridge. *Chemical Geology*, **171**(1-2): 49-75.
- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P. and Holm, N. (2002) Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36 Deg14'N, MAR). *Chemical Geology*, **191**(4): 345-359.
- Charlou, J.L., Donval, J.P., Konn, C., Ondreas, H., Fouquet, Y., Jean Baptiste, P. and Fourré, E. High production and fluxes of H₂ and CH₄ and evidence of abiotic hydrocarbon synthesis by serpentinization in ultramafic-hosted hydrothermal systems on the Mid-Atlantic Ridge. In: Rona, P., Devey, C., Dymont, J. and Murton, B., Diversity of Hydrothermal Systems on Slow-spreading Ocean Ridges. *Geophysical Monograph Series*, **InPress**.
- Charlou, J.L., Fouquet, Y., Bougault, H., Donval, J.P., Etoubleau, J., Jean-Baptiste, P., Dapoigny, A., Appriou, P. and Rona, P.A. (1998) Intense CH₄ plumes generated by serpentinization of ultramafic rocks at the intersection of the 15 Deg20'N fracture zone and the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta*, **62**(13): 2323-2333.

- Chekaliuk, E. B. (1971). The Thermodynamic Basis for the Theory of the Abiotic Genesis of Petroleum. Kiev, *Naukova Dumka* (in Russian).
- Chekaliuk, E. B. and J. F. Kenney (1991) The stability of hydrocarbons in the thermodynamic conditions of the Earth. *Proc. Am. Phys. Soc.* **36**(3): 347.
- Chen, Q.W. and Chen, C.L. (2005) The role of inorganic compounds in the prebiotic synthesis of organic molecules. *Current Organic Chemistry*, **9**(10): 989-998.
- Deamer, D., Dworkin, J.P., Sandford, S.A., Bernstein, M.P. and Allamandola, L.J. (2002) The First Cell Membranes. *Astrobiology*, **2**(4): 371-381.
- Ding, K. and Seyfried Jr, W.E. (1992) Determination of Fe-Cl complexing in the low pressure supercritical region (NaCl fluid): Iron solubility constraints on pH of subseafloor hydrothermal fluids. *Geochimica et Cosmochimica Acta*, **56**(10): 3681-3692.
- Douville, E., Charlou, J.L., Oelkers, E.H., Bienvvenu, P., Jove Colon, C.F., Donval, J.P., Fouquet, Y., Prieur, D. and Appriou, P. (2002) The rainbow vent fluids (36°14'N, MAR): the influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. *Chemical Geology*, **184**(1-2): 37.
- Ducluzeau, A.-L., van Lis, R., Duval, S., Schoepp-Cothenet, B., Russell, M.J. and Nitschke, W. (2009) Was nitric oxide the first deep electron sink? *Trends in Biochemical Sciences*, **34**(1): 9-15.
- Escartin, J., Smith, D.K., Cann, J., Schouten, H., Langmuir, C.H. and Escrig, S. (2008) Central role of detachment faults in accretion of slow-spreading oceanic lithosphere. *Nature*, **455**(7214): 790-794.
- Eglinton, G. and Calvin, M. (1967) Chemical fossils. *Scientific American*, **216**: 32-43
- Ferris, J.P. (1992) Chapter 6 Chemical markers of prebiotic chemistry in hydrothermal systems. *Origins of Life and Evolution of Biosphere*, **22**(1): 109-134.
- Ferris, J.P. (2005) Catalysis and Prebiotic Synthesis. *Reviews in Mineralogy and Geochemistry*, **59**: 187-210.
- Fiebig, J., Woodland, A.B., D'Alessandro, W. and Puttmann, W. (2009) Excess methane in continental hydrothermal emissions is abiogenic. *Geology*, **37**(6): 495-498.
- Fiebig, J., Woodland, A.B., Spangenberg, J. and Oschmann, W. (2007) Natural evidence for rapid abiogenic hydrothermal generation of CH₄. *Geochimica et Cosmochimica Acta*, **71**(12): 3028-3039.
- Forsman, J.P., and Hunt, J.M. (1958) Insoluble organic matter (kerogen) in sedimentary rocks of marine origin. In: Habitat of oil (ed. Weeks, L.G.), *American Association of Petroleum Geologists*, 747-778
- Fouquet, Y., Cherkashev, G., Charlou, J.L., Ondreas, H., Birot, D., Cannat, M., Bortnikov, N., Silantiev, S., Sudarikov, S., Cambon-Bonavita, M.-A., Desbruyères, D., Fabri, M.C., Querellou, J., Hourdez, S., Geybruk, A., Sokolova, T., Hoisé, E., Mercier, E., Konn, C., Donval, J., Etoubleau, J., Normand, A., Stephan, M., Briand, P., Crozon, J., Fernagu, P. and Buffier, E. (2008) Serpentine cruise - ultramafic hosted hydrothermal deposits on the Mid-Atlantic Ridge: First Submersible studies on Ashadze 1 and 2, Logatchev 2 and Krasnov fields. *InterRidge News*, **17**: 16-21.
- Foustoukos, D.I. and Seyfried, W.E., Jr. (2007) Fluid Phase Separation Processes in Submarine Hydrothermal Systems. *Reviews in Mineralogy and Geochemistry*, **65**(1): 213-239.
- Frost, B.R. and Beard, J.S. (2007) On Silica Activity and Serpentinization. *Journal of Petrology*, **48**(7): 1351-1368.
- Früh-Green, G.L., Kelley, D.S., Bernasconi, S.M., Karson, J.A., Ludwig, K.A., Butterfield, D.A., Boschi, C. and Proskurowski, G. (2003) 30,000 years of hydrothermal activity at the Lost City vent field. *Science*, **301**: 495-498.
- Gablina, I.F., Mozgova, N.N., Borodaev, Y.S., Stepanova, T.V. and Cherkashev, G.A. (2000) Copper Sulfide Associations in Recent Oceanic Ores of the Logachev Hydrothermal Field (Mid-Atlantic Ridge, 14°45'N). *Geology of Ore Deposits*, **42**(4): 296-316.
- German, C.R., Klinkhammer, G.P. and Rudnicki, M.D. (1996) The Rainbow Hydrothermal Plume, 36°15'N, MAR. *Geophysical Research Letters*, **23**(21): 2979-2982.
- Glasby, G.P. (2006) Abiogenic Origin of Hydrocarbons: An Historical review. *Resource Geology*, **56**(1): 83-96.
- Gold, T. (1992) The Deep, Hot Biosphere. *Proceedings of the National Academy of Sciences of the United States of America*, **89**(13): 6045-6049.
- Greenwell, H. and Coveney, P. (2006) Layered Double Hydroxide Minerals as Possible Prebiotic Information Storage and Transfer Compounds. *Origins of Life and Evolution of Biospheres*, **36**(1): 13.
- Hannington, M.D., de Ronde, C.E.J. and Petersen, S. (2005) Sea-Floor Tectonics and Submarine Hydrothermal Systems. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J. and Richards, J.P., *Economic Geology 100th Anniversary Volume*, pp. 111-142.

- Hoashi, M., Bevacqua, D.C., Otake, T., Watanabe, Y., Hickman, A.H., Utsunomiya, S. and Ohmoto, H. (2009) Primary haematite formation in an oxygenated sea 3.46 billion years ago. *Nature Geosciences*, **2**(4): 301-306.
- Holm, N.G. and Neubeck, A. (2009) Reduction of nitrogen compounds in oceanic basement and its implications for HCN formation and abiotic organic synthesis. (*submitted to Geochemical Transactions*).
- Huber, C. and Wächtershäuser, G. (2006) α -Hydroxy and α -Amino Acids Under Possible Hadean, Volcanic Origin-of-Life Conditions. *Science*, **314**(5799): 630-632.
- Ildefonse, B., Blackman, D.K., John, B.E., Ohara, Y., Miller, D.J., MacLeod, C.J. and Integrated Ocean Drilling Program Expeditions 304/305 Science Party (2007) Oceanic core complexes and crustal accretion at slow-spreading ridges. *Geology*, **35**(7): 623-626.
- Ildefonse, B., Fouquet, Y., Hoisé, E., Dyment, J., Gente, P., Thibaud, R., Bissedur, D., Yatheesh, V. and Party, M.S. (2008) Geological mapping of the Rainbow Massif, Mid-Atlantic Ridge, 36°14'N. *Eos, Transactions, American Geophysical Union*, **89**(53): T43B-2028.
- Ingmanson, D.E. and Dowler, M.J. (1977). *Origins of life*, **8**: 221-224.
- Kasting, J.F. (1990) Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Origins of Life and Evolution of Biosphere*, **20**(3): 199-231.
- Kasting, J.F. (2005) Methane and climate during the Precambrian era. *Precambrian Research*, **137**(3-4): 119-129.
- Kelley, D.S., Gillis, K.M. and Thompson, G. (1993) Fluid Evolution in Submarine Magma-Hydrothermal Systems at the Mid-Atlantic Ridge. *Journal of Geophysical Research*, **98**(B11)(19): 579-596.
- Kelley, D.S., Karson, J.A., Blackman, D.K., Fruh-Green, G.L., Butterfield, D.A., Lilley, M.D., Olson, E.J., Schrenk, M.O., Roe, K.K., Lebon, G.T., Rivizzigno, P. and the, A.T.S.P. (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30[deg] N. *Nature*, **412**(6843): 145-149.
- Kelley, D.S., Karson, J.A., Fruh-Green, G.L., Yoerger, D.R., Shank, T.M., Butterfield, D.A., Hayes, J.M., Schrenk, M.O., Olson, E.J., Proskurowski, G., Jakuba, M., Bradley, A., Larson, B., Ludwig, K., Glickson, D., Buckman, K., Bradley, A.S., Brazelton, W.J., Roe, K., Elend, M.J., Delacour, A., Bernasconi, S.M., Lilley, M.D., Baross, J.A., Summons, R.E. and Sylva, S.P. (2005) A Serpentinite-Hosted Ecosystem: The Lost City Hydrothermal Field. *Science*, **307**(5714): 1428-1434.
- Kenney, J.F. (1995) Comment on "Mantle hydrocarbons: Abiotic or biotic?" by R. Sugisaki and K. Mimura. *Geochimica et Cosmochimica Acta*, **59**(18): 3857-3858.
- Kenney, J.F. (1996) Considerations about recent prediction of impending shortages of petroleum evaluated from the perspective of modern petroleum science. *Special Edition on The Future of Petroleum: In Energy World, British Institute of Petroleum, London*.
- Kompanichenko, V.N. (2009) Changeable hydrothermal media as potential cradle of life on a planet. *Planetary and Space Science*, **57**(4): 468-476.
- Konhauser, K. (2009) Biogeochemistry: Deepening the early oxygen debate. *Nature Geosciences*, **2**(4): 241-242.
- Konn, C., Charlou, J., Donval, J. and Holm, N.G. (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 (36N, Mid-Atlantic ridge) over 3 years. *Submitted to Applied Geochemistry*.
- 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.
- Konn, C., Magnér, J., Charlou, J.L., Holm, N.G. and Alsberg, T. (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. *Submitted to Geochemical Transactions*.
- Konn, C., Testemale, D., Querellou, J., Holm, N.G. and Charlou, J.L. (Paper III) New insight on the origin of organic compounds in fluids from ultramafic-hosted hydrothermal systems. *Submitted to Geobiology*.
- Koonin, E.V. and Martin, W. (2005) On the origin of genomes and cells within inorganic compartments. *Trends in Genetics*, **21**(12): 647-654.
- Koschinsky, A., Garbe-Schonberg, D., Sander, S., Schmidt, K., Gennerich, H.-H. and Strauss, H. (2008) Hydrothermal venting at pressure-temperature conditions above the critical point of seawater, 5°S on the Mid-Atlantic Ridge. *Geology*, **36**(8): 615-618.
- Krayushkin, V.A., Tchebanenko, T.I., Klochko, V.P., Dvoryanin, Ye.S. and Kenney, J.F. (1994) Recent applications of the modern theory of abiogenic hydrocarbon origins: Drilling and development of oil & gas fields in the Dneiper-Donets Basin. *VIIth International Symposium on the Observation of the Continental Crust through Drilling, Santa Fe, NM, DOSECC: 21-24*.

- Lagabriele, Y., Bideau, D., Cannat, M., Karson, J.A. and Mevel, C. (1998) Ultramafic-mafic plutonic rock suites exposed along the Mid-Atlantic Ridge (10°N-30°N). Symmetrical-asymmetrical distribution and implications for seafloor spreading processes. In: Buck, W.R., Delaney, P.T., Karson, J.A. and Lagabriele, Y., Faulting and magmatism at midocean ridges. *American Geophysical Union Geophysical Monograph*.
- Lincoln, T.A. and Joyce, G.F. (2009) Self-Sustained Replication of an RNA Enzyme. *Science*, **323**(5918): 1229-1232.
- Mahfoud, R.F. (1991) Inorganic origin in upper mantle seen likely for solid hydrocarbon in Syria basalt. *Oil & Gas Journal*, **October 28**.
- Mahfoud, R.F. and Beck, J. N. (1995) Why the Middle East fields may produce oil forever. *Offshore*, **106**: 58-64.
- Mango, F., Jarvie, D. and Herriman, E. (2009) Natural gas at thermodynamic equilibrium: Implications for the origin of natural gas. *Geochemical Transactions*, **10**(1): 6.
- Marshall, W.L. (1994) Hydrothermal synthesis of amino acids. *Geochimica et Cosmochimica Acta*, **58**(9): 2099.
- Martin, R.S., Mather, T.A. and Pyle, D.M. (2007) Volcanic emissions and the early Earth atmosphere. *Geochimica et Cosmochimica Acta*, **71**(15): 3673-3685.
- Martin, W. and Russell, M.J. (2007) Review. On the origin of biochemistry at an alkaline hydrothermal vent. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **362**(1486): 1887-1925.
- McCaig, A.M., Cliff, R.A., Escartin, J., Fallick, A.E. and MacLeod, C.J. (2007) Oceanic detachment faults focus very large volumes of black smoker fluids. *Geology*, **35**(10): 935-938.
- McCollom, T.M. (2000) Experimental investigation of abiotic synthesis of organic compounds under hydrothermal conditions. *Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000*: GEOC-028.
- McCollom, T.M. and Bach, W. (2009) Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta*, **73**(3): 856-875.
- McCollom, T.M., Ritter, G. and Simoneit, B.R.T. (1999) Lipid Synthesis Under Hydrothermal Conditions by Fischer-Tropsch-Type Reactions. *Origins of Life and Evolution of Biosphere*, **29**(2): 153-166.
- McCollom, T.M. and Seewald, J.S. (2001) A reassessment of the potential for reduction of dissolved CO₂ to hydrocarbons during serpentinization of olivine. *Geochimica et Cosmochimica Acta*, **65**(21): 3769-3778.
- McCollom, T.M. and Seewald, J.S. (2007) Abiotic Synthesis of Organic Compounds in Deep-Sea Hydrothermal Environments. *Chemical Reviews*, **107**(2): 382-401.
- McCollom, T.M. and Simoneit, B.R. (1999) Abiotic formation of hydrocarbons and oxygenated compounds during thermal decomposition of iron oxalate. *Origins of life and evolution of the biosphere*, **29**(2): 167-86.
- Melchert, B., Devey, C.W., German, C.R., Lackschewitz, K.S., Seifert, R., Walter, M., Mertens, C., Yoerger, D.R., Baker, E.T., Paulick, H. and Nakamura, K. (2008) First evidence for high-temperature off-axis venting of deep crustal/mantle heat: The Nibelungen hydrothermal field, southern Mid-Atlantic Ridge. *Earth and Planetary Science Letters*, **275**(1-2): 61-69.
- Mogarovskiy, V., Budanovak K.T. and Dmitriyev E.A. (1980) The geochemistry of carbon in magmatic and metamorphic rocks of the Pamirs. *Proceedings Annals Ukr.S.S.R., Series B, No. 2* (in Russian and Ukrainian)
- Moldowan, J.M. and Seifert, W.K. (1979) Head-to-Head Linked Isoprenoid Hydrocarbons in Petroleum. *Science*, **204**: 169-171
- Mottl, M.J. and Holland, H.D. (1978) Chemical exchange during hydrothermal alteration of basalt by seawater--I. Experimental results for major and minor components of seawater. *Geochimica et Cosmochimica Acta*, **42**(8): 1103.
- Murton, B.J., Klinkhammer, G., Becker, K., Briaies, A., Edge, D., Hayward, N., Millard, N., Mitchell, I., Rouse, I., Rudnicki, M., Sayanagi, K., Sloan, H. and Parson, L. (1994) Direct evidence for the distribution and occurrence of hydrothermal activity between 27°N-30°N on the Mid-Atlantic Ridge. *Earth and Planetary Science Letters*, **125**(1-4): 119-128.
- Nagaseki, H. and Hayashi, K.-i. (2008) Experimental study of the behavior of copper and zinc in a boiling hydrothermal system. *Geology*, **36**(1): 27-30.
- Nelson, K.E., Levy, M. and Miller, S.L. (2000) Peptide nucleic acids rather than RNA may have been the first genetic molecule. *Proceedings of the National Academy of Sciences of the United States of America*, **97**(8): 3868-3871.
- O'Hanley, D.S. (1996) Serpentinites: Records of Tectonic and Petrological History. *Oxford Monographs on Geology and Geophysics* **34**. Oxford University Press, USA 277 pp.

- Ondreas, H., Cannat, M., Cherkashev, G., Fouquet, Y., Normand, A. and Serpentine Scientific Party, A. (2007) High Resolution Mapping of the Ashadze and Logachev Hydrothermal Fields, Mid Atlantic Ridge 13-15°N. *Eos, Transactions, American Geophysical Union*, **88**(52): T53B-1310.
- Pavlov, A.A., Kasting, J.F., Brown, L.L., Rages, K.A. and Freedman, R. (2000) Greenhouse warming by CH₄ in the atmosphere of early Earth. *Journal of Geophysical Research*, **105**: 11981-11990.
- Penner, S. (2006) Biogenic v. Abiogenic Oil: Will Worldwide Production Peak? *Doctors for Disasters Preparation, 2006 Annual Meeting - Portland, OR*: <http://www.ddponline.org/node/9> (direct link to audio material <http://ia360939.us.archive.org/3/items/DDP24th06Penner/06penner.mp3>).
- Petersen, S., Kuhn, K., Kuhn, T., Augustin, N., Hékinian, R., Franz, L. and Borowski, C. (2009) The geological setting of the ultramafic-hosted Logatchev hydrothermal field (14°45'N, Mid-Atlantic Ridge) and its influence on massive sulfide formation. *Lithos*, **In Press**.
- Peterson, A.A., Vogel, F., Lachance, R.P., Froling, M., Antal, M.J., Jr. and Tester, J.W. (2008) Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy & Environmental Science*, **1**(1): 32-65.
- Pokrovski, G.S., Roux, J. and Harrichoury, J.-C. (2005) Fluid density control on vapor-liquid partitioning of metals in hydrothermal systems. *Geology*, **33**(8): 657-660.
- Porfir'yev, V.B. (1956) *All-Union Conference on Petroleum and Petroleum Geology, Moscow*.
- Pontes-Buarque, M., Tassis, A.C., Bonapace, J.A.P., Monte, M.B.M., De Souza-Barros, F. and Vieyra, A. (2000) Surface charges and interfaces: Implications for mineral roles in prebiotic chemistry. *Anais da Academia Brasileira de Ciencias*, **72**(3): 317-322.
- Proskurowski, G., Lilley, M.D., Kelley, D.S. and Olson, E.J. (2006) Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope geothermometer. *Chemical Geology*, **229**(4): 331.
- Proskurowski, G., Lilley, M.D., Seewald, J.S., Fruh-Green, G.L., Olson, E.J., Lupton, J.E., Sylva, S.P. and Kelley, D.S. (2008) Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field. *Science*, **319**(5863): 604-607.
- Rosing, M.T. (1999) 13C-Depleted Carbon Microparticles in >3700-Ma Sea-Floor Sedimentary Rocks from West Greenland. *Science*, **283**(5402): 674-676.
- Rushdi, A.I. and Simoneit, B.R.T. (2001) Lipid Formation by Aqueous Fischer-Tropsch-Type Synthesis over a Temperature Range of 100 to 400°C. *Origins of Life and Evolution of Biosphere*, **31**(1-2): 103-118.
- Rushdi, A.I. and Simoneit, B.R.T. (2004) Condensation Reactions and Formation of Amides, Esters, and Nitriles Under Hydrothermal Conditions. *Astrobiology*, **4**(2): 211-224.
- Rushdi, A.I. and Simoneit, B.R.T. (2005) Abiotic Synthesis of Organic Compounds from Carbon Disulfide Under Hydrothermal Conditions. *Astrobiology*, **5**(6): 749-769.
- Rushdi, A.I. and Simoneit, B.R.T. (2006) Abiotic Condensation Synthesis of Glyceride Lipids and Wax Esters Under Simulated Hydrothermal Conditions. *Origins of Life and Evolution of Biospheres*, **36**(2): 93.
- Russell, M.J. and Arndt, N.T. (2005) Geodynamic and metabolic cycles in the Hadean. *Biogeosciences*, **2**(1): 97-111.
- Russell, M.J. and Hall, A.J. (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *Journal of the Geological Society*, **154**(3): 377-402.
- Russell, M.J., Hall, A.J., Boyce, A.J. and Fallick, A.E. (2005) 100th Anniversary Special Paper: On Hydrothermal Convection Systems and the Emergence of Life. *Economic Geology*, **100**(3): 419-438.
- Russell, M.J., Hall, A.J., Cairns-Smith, A.G. and Braterman, P.S. (1988) Submarine hot springs and the origin of life. *Nature*, **336**(6195): 117-117.
- Schmidt, K., Koschinsky, A., Garbe-Schonberg, D., de Carvalho, L.M. and Seifert, R. (2007) Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-Atlantic Ridge: Temporal and spatial investigation. *Chemical Geology*, **242**(1-2): 1.
- Schoonen, M., A. A., Xu, Y. and Bebie, J. (1999) Energetics and Kinetics of the Prebiotic Synthesis of Simple Organic Acids and Amino Acids with the FeS-H₂S/FeS₂ Redox Couple as Reductant. *Origins of Life and Evolution of Biosphere*, **29**(1): 5.
- Schoonen, M.A.A. and Xu, Y. (2001) Nitrogen Reduction Under Hydrothermal Vent Conditions: Implications for the Prebiotic Synthesis of C-H-O-N Compounds. *Astrobiology*, **1**(2): 133-142.
- Scott, R.B., Rona, P.A., McGregor, B.A. and Scott, M.R. (1974) The TAG hydrothermal field. *Nature*, **251**(5473): 301-302.
- Seewald, J.S., Zolotov, M.Y. and McCollom, T. (2006) Experimental investigation of single carbon compounds under hydrothermal conditions. *Geochimica et Cosmochimica Acta*, **70**(2): 446.

- Segré, D., Ben-Eli, D., Deamer, D., W. and Lancet, D. (2001) The Lipid World. *Origins of Life and Evolution of Biosphere*, **31**(1): 119.
- Serpentine-Cruise-Ifremer, 2007. Serpentine cruise.
- Sherwood Lollar, B., Westgate, T.D., Ward, J.A., Slater, G.F. and Lacrampe-Couloume, G. (2002) Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs. *Nature*, **416**(6880): 522-524.
- Shock, E.L. (1990) Geochemical constraints on the origin of organic compounds in hydrothermal systems. *Origins of Life and Evolution of Biosphere*, **20**(3): 331.
- Shock, E.L. and Schulte, M.D. (1998) Organic synthesis during fluid mixing in hydrothermal systems. *Journal of Geophysical Research*, **103**(E12): 28, 513.
- Simoneit, B.R.T. (1995) Evidence for organic synthesis in high temperature aqueous media - Facts and prognosis. *Origins of Life and Evolution of Biosphere*, **25**(1): 119.
- Sugisaki R. and Mimura K. (1994) Mantle hydrocarbons: Abiotic or biotic? *Geochemica Cosmochimica Acta*, **58**: 2527-2542.
- Summons, R.E. and Jahnke, L.L. (1992) Hopanes and hopanes methylated in ring-A: correlation of the hopanoids of extant methylotrophic bacteria with their fossil analogues. In: Biomarkers in Sediments and Petroleum (eds. Moldowan J.M. , Albrecht P. & Philp R. P.), *Prentice Hall, NJ*, 182-200.
- Szatmari, P. (1989) Petroleum formation by Fischer-Tropsch synthesis in plate tectonics. *AAPG Bulletin*, **73**(8): 989-998.
- Takai, K., Gamo, T., Tsunogai, U., Nakayama, N., Hirayama, H., Nealson, K.H. and Horikoshi, K. (2004) Geochemical and microbiological evidence for a hydrogen-based, hyperthermophilic subsurface lithoautotrophic microbial ecosystem (HyperSLiME) beneath an active deep-sea hydrothermal field. *Extremophiles*, **8**(4): 269-82.
- Tissot, B.P. and Welte, D.H. (1984) Petroleum Formation and Occurrence. *Springer Verlag*.
- The New York Times (2007) Brazil Discovers an Oil Field Can Be a Political Tool, **November 19**.
- Van Dover, C.L., German, C.R., Speer, K.G., Parson, L.M. and Vrijenhoek, R.C. (2002) Evolution and Biogeography of Deep-Sea Vent and Seep Invertebrates. *Science*, **295**(5558): 1253-1257.
- Walde, P. (2006) Surfactant Assemblies and their Various Possible Roles for the Origin(s) of Life. *Origins of Life and Evolution of Biospheres*, **36**(2): 109.
- Watanabe, M., Sato, T., Inomata, H., Smith, R.L., Arai, K., Kruse, A. and Dinjus, E. (2004) Chemical Reactions of C1 Compounds in Near-Critical and Supercritical Water. *Chemical Reviews*, **104**(12): 5803-5822.
- Wetzel, L.R. and Shock, E.L. (2000) Distinguishing ultramafic- from basalt-hosted submarine hydrothermal systems by comparing calculated vent fluids compositions. *Journal of Geophysical Research*, **105**(B4): 8319-8340.
- Wilde, S.A., Valley, J.W., Peck, W.H. and Graham, C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, **409**(6817): 175-178.
- Wilson, C.T.R. (1897) Condensation of Water Vapour in the Presence of Dust-Free Air and Other Gases. *Philosophical Transactions of the Royal Society of London. Series A*, **189**: 265-307.