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Hydrothermal exploration and astrobiology: oases for life in distant oceans?

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Abstract: High-temperature submarine hydrothermal fields on Earth's mid-ocean ridges play host to exotic ecosystems with fauna previously unknown to science. Because these systems draw significant energy from *chemo*synthesis rather than *photo*synthesis, it has been postulated that the study of such systems could have relevance to the origins of life and, hence, astrobiology. A major flaw to that argument, however, is that modern basalt-hosted submarine vents are too oxidizing and lack the abundant free hydrogen required to drive abiotic organic synthesis and/or the energy yielding reactions that the most primitive anaerobic thermophiles isolated from submarine vent-sites apparently require. Here, however, the progress over the past decade in which systematic search strategies have been used to identify previously overlooked venting on the slow-spreading Mid-Atlantic Ridge and the ultra-slow spreading Arctic and SW Indian Ridges is described. Preliminary identification of fault-controlled venting in a number of these sites has led to the discovery of at least two high-temperature hydrothermal fields hosted in ultramafic rocks which emit complex organic molecules in their greater than 360 °C vent-fluids. Whether these concentrations represent *de novo* organic synthesis within the hydrothermal cell remains open to debate but it is probable that many more such sites exist throughout the Atlantic, Arctic and SW Indian Oceans. One particularly intriguing example is the Gakkel Ridge, which crosses the floor of the Arctic Ocean. On-going collaborations between oceanographers and astrobiologists are actively seeking to develop a new class of free-swimming autonomous underwater vehicle, equipped with appropriate chemical sensors, to conduct long-range missions that will seek out, locate and investigate new sites of hydrothermal venting at the bottom of this, and other, ice-covered oceans.

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Introduction

The first identification of submarine hydrothermal vents and their accompanying chemosynthetically-based communities in the late 1970s remains one of the most exciting discoveries in modern science (see, e.g., Van Dover 2000; German & Von Damm 2003). The existence of some form of hydrothermal circulation had been predicted almost as soon as the significance of ridges themselves was first recognized, with the emergence of plate tectonic theory. Hydrothermal circulation occurs when seawater percolates downwards through fractured ocean crust along the volcanic mid-ocean ridge system. The seawater is first heated and then undergoes chemical modification through reaction with the host rock as it continues downwards, reaching maximum temperatures which can exceed 400 °C. At these temperatures the fluids become extremely buoyant and rise rapidly back to the seafloor where they are expelled into the overlying water column (Fig. 1). Twenty-five years after its first discovery, seafloor hydrothermal circulation is increasingly recognized as playing a significant role in the cycling of energy and mass between the solid Earth and the oceans (German & Von Damm 2003).

While recent work has now established that hydrothermal activity is present in all ocean basins, however, and can occur along all forms of mid-ocean ridge spreading centre, it remains the case that less than 10 % of the global ridge crest has yet been explored systematically for seafloor hydrothermal venting (Baker & German 2004). This is of particular interest to marine biologists interested in understanding the biogeography and biodiversity of the exotic chemosynthetic fauna found at hydrothermal vent-sites. To that end, a major programme of the Census of Marine Life has now been dedicated to the exploration of key sections of ridge crest to investigate the potential for gene-flow between – and/or completely isolated evolution of – vent-fauna inhabiting a range of settings around the (still largely unexplored) global ridge system. In this paper, the focus is primarily upon recent hydrothermal discoveries along some of the world's least volcanically active

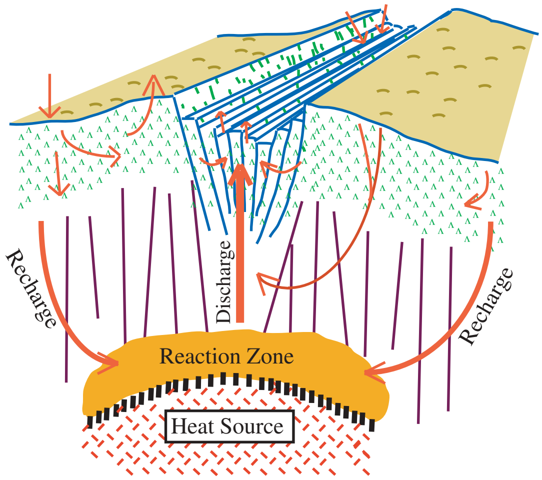

Fig. 1. A schematic illustration of the three key stages of submarine hydrothermal circulation through young ocean crust (after Alt 1995). Seawater enters the crust in widespread 'recharge' zones and reacts under increasing conditions of temperature and pressure as it penetrates downwards. Maximum temperatures and pressures are experienced in the 'reaction zone', close to the (magmatic or hot-rock) 'heat source' before buoyant plumes rise rapidly back toward the seafloor – the 'discharge' zone.

ridge crests, the unique chemical compositions of the vent-fluids that result and their potential relevance for astrobiology.

Hydrothermal activity and the origins of life

Chemosynthetic vent-fauna

Upon first discovery, links were rapidly made to whether submarine hydrothermal systems might represent circumstances similar to those essential to the origins of life (see, e.g., Corliss 1986). A driving factor in such speculations was that hydrothermal vent systems play host to unique life forms previously unknown to science which, at the base of their food chain, rely upon the chemical energy available from the interaction between reduced compounds in hydrothermal vent-fluids (e.g. H_2S, CH_4) and the overlying, more oxidizing seawater. For this reason, these systems became known as *chemo*synthetic ecosystems (as opposed to *photo*synthetic ecosystems). Since their first discovery in 1977, more than 450 species of hydrothermal vent-fauna have been identified that are new to science – at an average rate of more than one new species every two weeks throughout that quarter-century or more (Van Dover *et al.* 2002). When studied in detail, these fauna reveal six quite distinct biogeographic provinces in the Atlantic, Pacific and Indian Oceans (Fig. 2). What is interesting to note at the same time, however, is that the basic compositions of both the seawater and the basalt (the primary reactants in most hydrothermal systems in all of these areas) are broadly very similar to one another, even though the fauna that occupy these different vent-sites quite clearly differ, markedly, one from another (Van Dover 2000; Van Dover *et al.* 2002).

The notion that submarine hydrothermal systems fuelled by chemical energy independent of sunlight could sustain lush 'oasis-like' ecosystems is an attractive one to astrobiologists because any other planetary system hosting volcanism and a body of liquid water might be expected to also host hydrothermal systems. Furthermore, the combination of heat and chemicals thermodynamically available for energy yielding reactions, all in an aquatic environment, appears tantalizingly close to Darwin's original 'warm little pond' hypothesis (Darwin 1959) – perhaps the first exposition of the concept of putative 'primordial soup'. Subsequent work has both strengthened and weakened arguments for any links between submarine hydrothermal activity and the origins of life on Earth – with direct implications for astrobiological exploration.

The last common ancestor

One important concept is the notion of the *last* common ancestor for life on Earth. This can usefully be conceived of as the last cell or cluster of cells from which all modern cells are descended (Woese 1999). The common view is that this last common ancestor was an anaerobic thermophile (Fig. 3) living in hot conditions (>85 °C) and probably in close proximity to some hydrothermal system (Stetter 1996; Nisbet & Fowler 1996a, b; Miyazaki *et al.* 2001). Geologic arguments in favour of these suggestions include: (i) hydrothermal systems provide a range of potential thermodynamic drivers for prephotosynthetic life; (ii) metals that are abundant in hydrothermal systems (e.g. Fe, Co, Ni, Zn) are also a requirement of (presumably ancient) enzymes responsible for cells' biochemical maintenance; and (iii) heat-shock proteins are integral to protein shaping, suggesting that heat-shock may have been a common problem to early life (Nisbet & Fowler 2003). While some (e.g. Forterre 1996; Glansdorff 2000; Brochier & Philippe 2002) have suggested some milder mesophilic origin for the last common ancestor, what does seem clear is that prephotosynthetic organisms would have depended on natural redox contrasts and, therefore, would have had to live in environments where such contrasts were accessible. A geologic scenario that might reconcile all of these opinions would be if the last common ancestor lived on the periphery (~40 °C) of a hotter hydrothermal system and that it was cells that strayed into those hotter settings that slowly adapted into hyperthermophiles (Nisbet & Fowler 2003).

The importance of free hydrogen

Even if the above arguments hold true for the origins of life on early Earth, however, there is a fundamental weakness in arguing for the relevance of modern hydrothermal systems hosted in basaltic mid-ocean ridges when considering such processes. Half a century ago, and approximately a quarter of a century before the discovery of seafloor hydrothermal venting, Miller (1953) had already demonstrated that a combination of methane, hydrogen and ammonia in the presence of water could be induced, in an apparatus with discharging electricity, to yield 13 of the 21 amino acids essential to life.

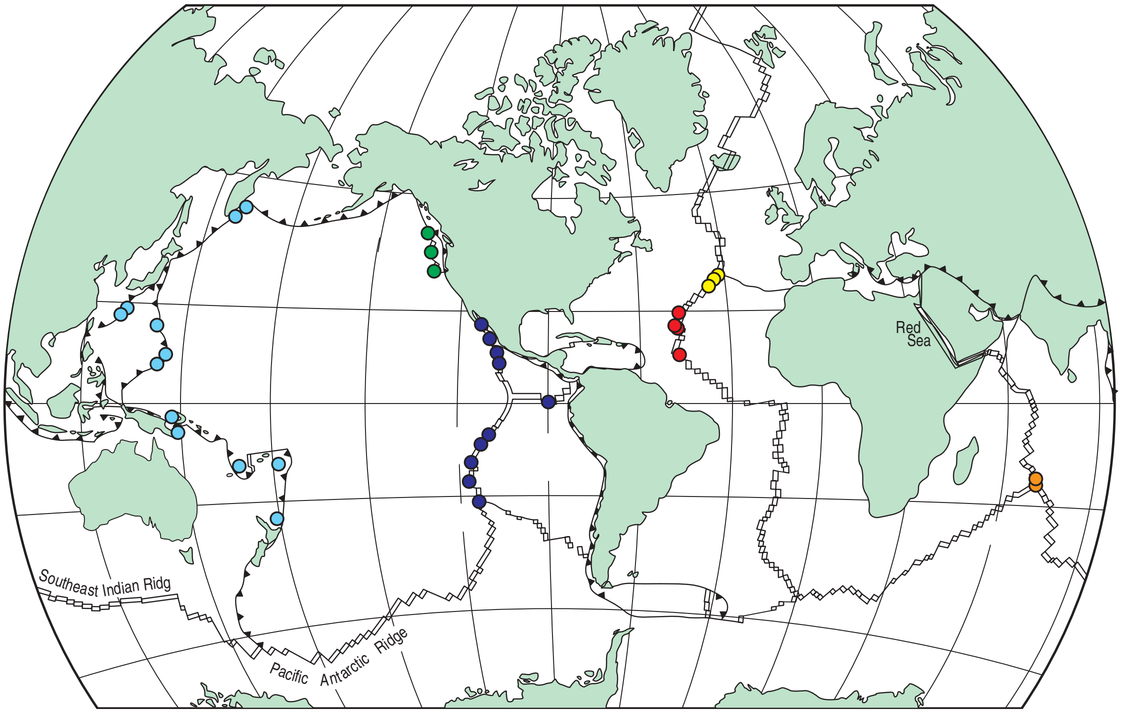

Fig. 2. A map of known hydrothermal vent biogeographic provinces and major mid-ocean ridges (after Van Dover *et al*. 2002). Pale blue, western Pacific; green, northeast Pacific; dark blue, East Pacific Rise; yellow, Azores; red, Mid-Atlantic Ridge; orange, Indian Ocean.

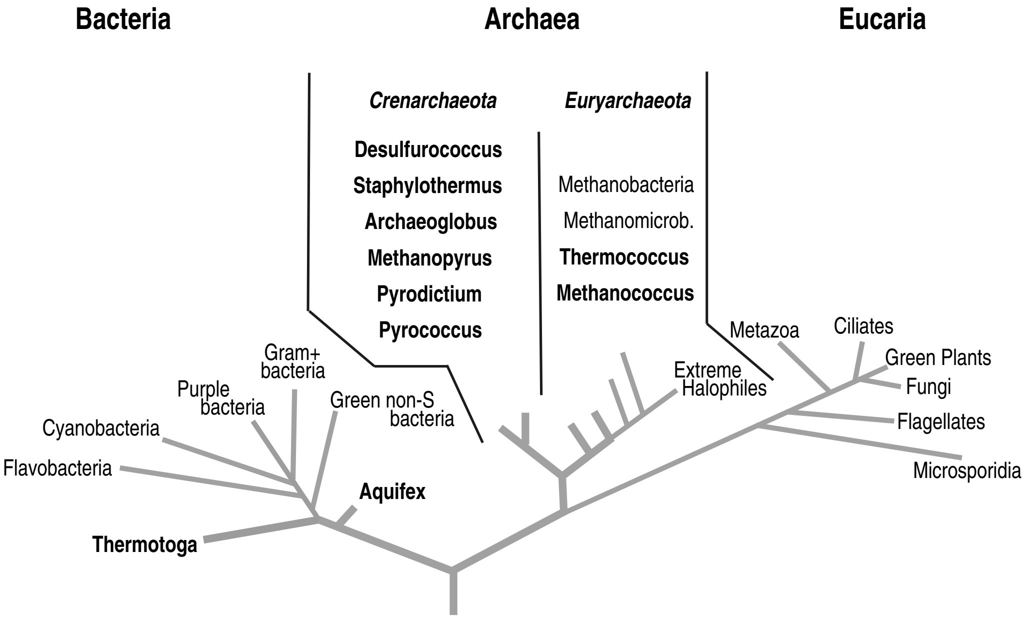

Fig. 3. The major marine genera of hyperthermophilic archaea and bacteria, isolated from hydrothermal vents (after Jannasch 1997), superimposed in bold upon the 16S rRNA-based phylogenetic tree of Woese (1999).

While modern hydrothermal vents may host numerous extremophiles, however, one extreme view is that these systems may be quite irrelevant to the synthesis of organic compounds essential to life because the conditions prevailing at such locations would be more likely to decompose, rather than enhance, any prebiotic chemistry (Miller 2003). While complex biochemistry can apparently spring from simpler building blocks, one essential component apparently absent from modern submarine hydrothermal systems is hydrogen (e.g. Von Damm 1995). This was elucidated particularly clearly by Jannasch (1997) who demonstrated that a number of the submarine hyperthermophilic archaea closest to the base of Woese's 'tree of life' (Fig. 3), together with the similarly 'primitive' bacterium *Aquifex Sulfolobus*, all catalysed

Table 1. *Energy-yielding reactions catalysed by submarine vent hyperthermophiles* (*after Jannasch 1997*)

Electron donor	Electron accelerator	Reaction	Organisms
H_2	CO_2	$4H_2+CO_2=CH_4+2H_2O$	Methanopyrus Methanococcus
H_2	S^0	$H_2+S^0=H_2S$	Pyrodictium[1]
H_2	SO_4^{2-}, $S_2O_3^{2-}$	$4H_2+H_2SO_4=H_2S+4H_2O$	Archaeoglobus[1]
S^{2-}; S^0	O_2	$2H_2+O_2=2H_2O$ $2S^0+3O_2+2H_2O=2H_2SO_4$	 Aquifex Sulfolobus[2]

[1] Facultatively heterotrophic.

[2] Not yet isolated from submarine hydrothermal systems.

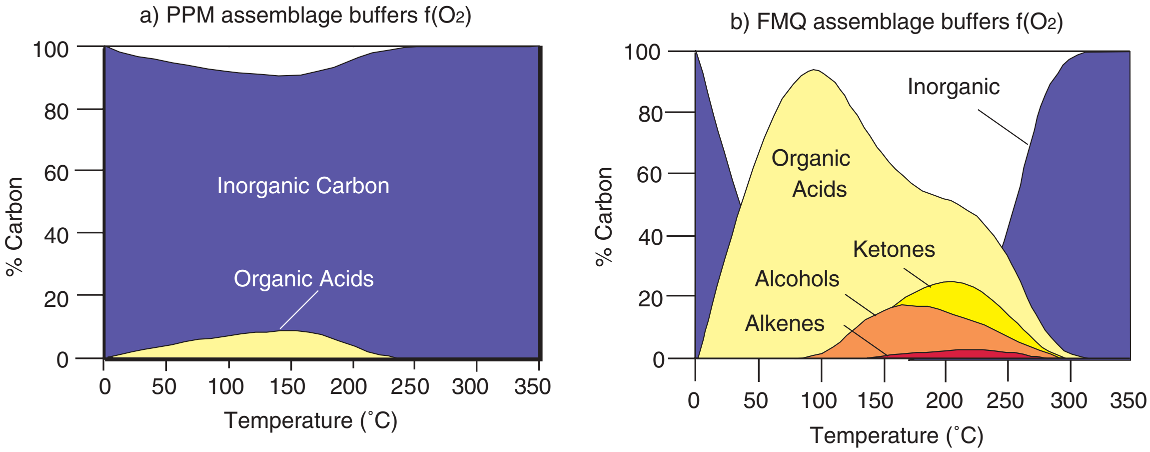

Fig. 4. The calculated distribution of carbon during mixing of hypothetical early-Earth seawater and hydrothermal vent-fluid, using fluids with different initial oxidation states (after Shock & Schulte 1998): (a) results for mixing seawater and a vent-fluid with an initial oxidation state set by the PPM assemblage representative of MORB-hosted hydrothermal activity; (b) results for mixing seawater and a vent-fluid with an initial oxidation state set by the FMQ assemblage representative of ultramafic-hosted hydrothermal activity.

energy-yielding chemosynthetic reactions that could only proceed in the presence of free hydrogen (Table 1). At that time, some 20 years after the first discovery of seafloor hydrothermal systems, fluids rich in dissolved hydrogen had not been found at any vent-site except the Guaymas Basin, Gulf of California – a special case of a ridge-crest being buried by sediments rich in *photosynthetically*-derived organic matter (Von Damm 1995).

Potential for hydrothermal organic synthesis

A detailed chemical consideration of this same problem was laid out quasi-contemporaneously by Shock and Schulte (1998) in a study that aimed to evaluate the prospects for abiotic organic synthesis during fluid mixing in hydrothermal systems. Their study was targeted primarily at situations likely on the early Earth and Mars and highlighted that the potential for organic synthesis is a strong function of the H_2 content of the source hydrothermal fluid which, in turn, is determined by the prevailing oxidation state – essentially a function of the rocks that host the hydrothermal system. First, Shock and Schulte (1998) considered the situation for hydrothermal fluids at 350 °C in equilibrium with the pyrrhotite–pyrite–magnetite (PPM) mineral assemblage, taken to be closely consistent with modern basalt-hosted submarine hydrothermal fluids (e.g. Haymon & Kastner 1981; Janecky & Seyfried 1984). The resultant thermodynamic calculations revealed that, upon mixing with ambient seawater, modern hydrothermal fluids could, indeed, be expected to generate some small proportion of organic acids at temperatures between 50 and 200 °C encompassing the known range for thermophilic archaea and bacteria. When the same calculations were repeated for hypothesized 'early Earth' seawater (similar in composition to modern seawater, but without dissolved oxygen) very similar results were obtained, except that the potential for organic synthesis was slightly greater and extended to slightly lower temperatures (Fig. 4(a)). While those results might be considered to be of at least some significance, what proved to be of much greater interest for astrobiological considerations were the results obtained from calculations for equilibration with the fayalite–magnetite–quartz (FMQ) mineral assemblage (Fig. 4(b)). The motivation for these studies was to consider the case for Hadean (early-Earth, ~4.56–4.0 Ga) hydrothermal systems hosted in higher eruption temperature (hence more Mg-rich) komatiitic lavas. In such circumstances, the initial oxidation state would be at or below values set by equilibrium with the FMQ assemblage. As can be seen (only the most oxidizing results from Shock and Schulte's work are reproduced in Fig. 4(b))

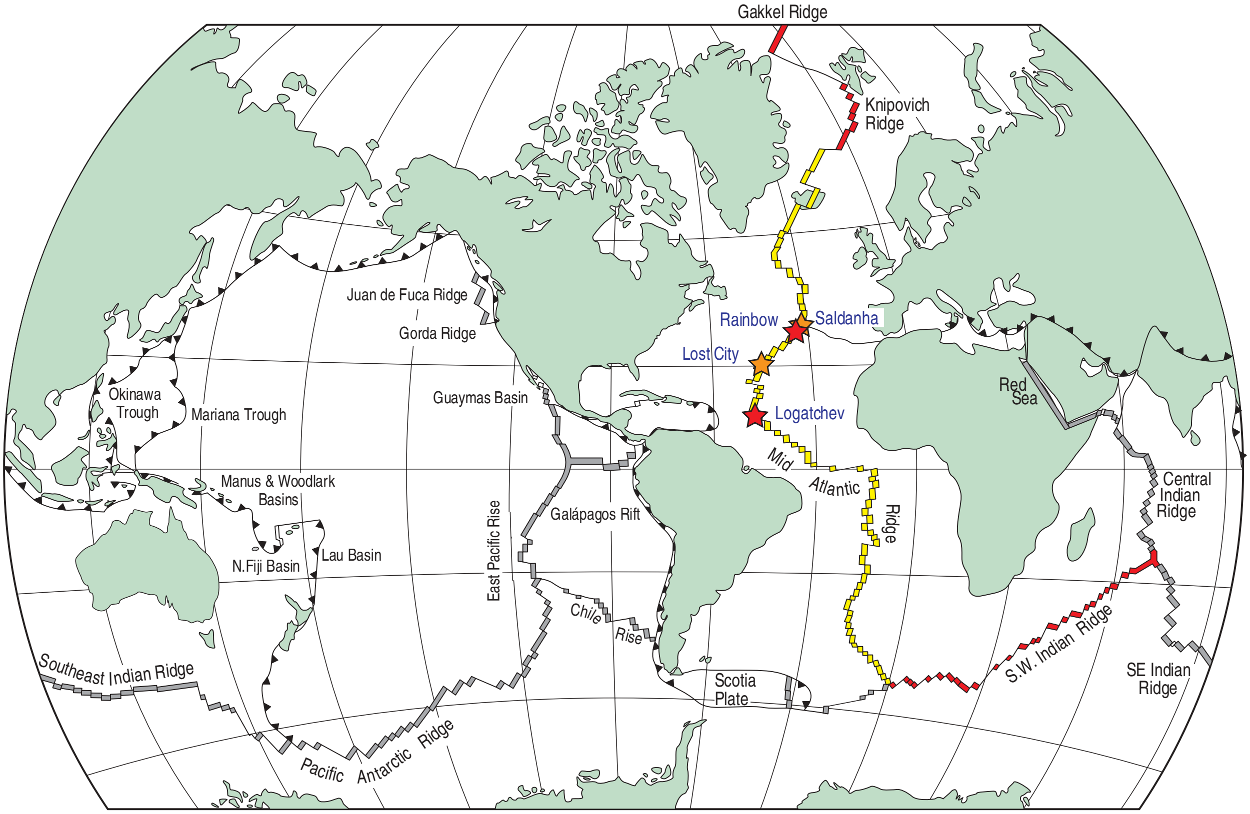

Fig. 5. A map of the major mid-ocean ridges highlighting the slow-spreading Mid-Atlantic Ridge (yellow) and, in red, the ultra-slow spreading Arctic (Gakkel, Knipovich) and SW Indian Ridges. Red stars show the locations of the Rainbow and Logatchev sites – both known high-temperature hydrothermal systems hosted in ultramafic rocks (see the text for a discussion). Saldanha and Lost City (orange stars) are low-temperature ultramafic-hosted hydrothermal fields.

the differences from basalt-hosted submarine systems are dramatic. For FMQ-buffered hydrothermal fluids, organic synthesis becomes important below 300 °C and at temperatures ranging between 170 and 110 °C essentially *quantitative* conversion from inorganic carbon to organic carbon is predicted to occur. Under more reducing conditions (not illustrated here) the corresponding temperature range over which organic molecules dominate becomes progressively broader (Shock & Schulte 1998). The implications for this work are immediately clear: for modern hydrothermal systems hosted in relatively oxidizing basaltic environments, organic synthesis is not favoured. Significant potential for abiotic organic synthesis would be expected, however, at any submarine hydrothermal systems hosted in ultramafic lithologies.

Slow-spreading ridges and the potential for organic synthesis at vent-sites

Hydrothermal activity and ridge-spreading rate

The recognition (above) that organic synthesis might accompany hydrothermal circulation through ultramafic lithologies coincided with a new international initiative to investigate whether hydrothermal circulation might occur along the Earth's very slowest-spreading mid-ocean ridges. Earlier work had suggested that the abundance of seafloor venting should occur in direct proportion to the rate of magma supply beneath any given ridge crest which, to a first approximation, is reflected by the ridge spreading rate (Baker *et al.* 1996). According to such a model, venting should be most abundant along the fastest-spreading ridges of the Pacific Ocean, but much less abundant – or perhaps even absent – along that 50% of the world's ridge crests that run South along the length of the Mid-Atlantic Ridge (MAR) from the Arctic to the Antarctic and then sweep eastward, South of South Africa into the SW Indian Ocean (Fig. 5). To test this hypothesis, a global programme of hydrothermal exploration was implemented with a particular emphasis on slow and ultra-slow spreading ridges (Baker & German 2004). Before discussing the significance of those findings, however, the systematic hydrothermal exploration strategies developed over the past decade that have allowed our hypotheses to be tested are first described.

The dynamics of deep-ocean hydrothermal plumes

When hot vent-fluids enter the base of the cold, stratified, ocean they are buoyant and begin to rise. Turbulent mixing leads to entrainment of 'background' material from the ambient water column within this rising plume. Because the oceans exhibit stable density-stratification, this mixing causes the buoyant plume to become progressively more diluted by water that is denser than both the initial vent-fluid *and* the overlying water column into which the plume is rising. The

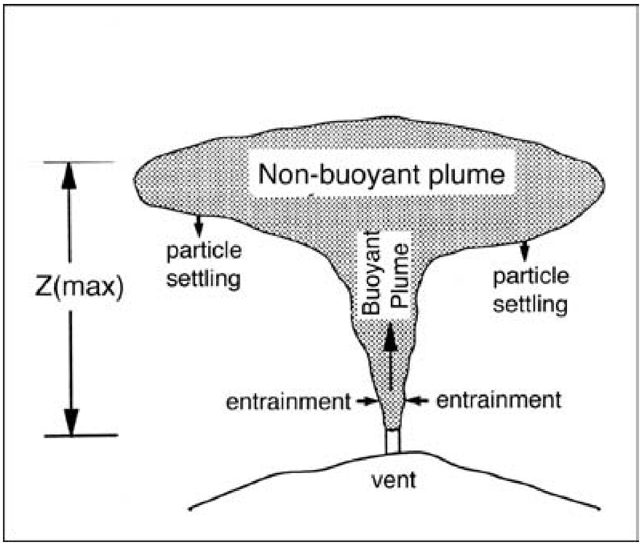

Fig. 6. Sketch of the hydrothermal plume rising above an active hydrothermal vent (after Helfrich & Speer 1995) illustrating entrainment of ambient seawater into the buoyant hydrothermal plume and establishment of a non-buoyant plume at a height $z_{\max}$.

plume, therefore, becomes progressively less buoyant as it rises, until it reaches some finite maximum height above the seafloor beyond which it cannot rise (Fig. 6). The exact height attained by the *non-buoyant* portion of any hydrothermal plume ($z_{\max}$) is a complex function of the initial buoyancy of the source vent-fluids and the degree of stratification of the water column into which they are injected, but in Earth's oceans these heights of rise typically range from $z_{\max} \leqslant 350$ m in the weakly stratified Atlantic Ocean to $z_{\max} \leqslant 150$ m in the more strongly stratified Pacific Ocean. For a typical plume, mixing also results in very rapid dilution of the primary vent-fluid (10^2–10^3:1) within the first 5–10 m of plume rise and even greater dilution ($\sim 10^4$:1) by the time of emplacement within the non-buoyant plume (Helfrich & Speer 1995). However, because hydrothermal vent-fluids can be up to 10^6-fold enriched over ordinary seawater in key tracers (notably Fe, Mn and CH_4), even the extensive dilution that occurs during rapid plume rise ($\leqslant$1 h to reach non-buoyant plume height) can still yield hydrothermal plume waters that are 100-fold enriched over background in those key tracers. This is important because, once emplaced at a height of neutral buoyancy, hydrothermal plumes tend to be dispersed by ambient deep-ocean currents and can readily be traced, using chemical techniques, over distances up to 50 km through the water column (German *et al.* 1998a). Thus, hydrothermal plumes provide a much greater spatial 'footprint' above any section of mid-ocean ridge crest than the high-temperature vent-fields that source them (typically $\leqslant$100 m across). Taking advantage of these characteristics of hydrothermal plumes provides the key to systematic exploration for hydrothermal activity along previously unexplored sections of the global ridge crest. A particular advantage is that dissolved Fe released into these hydrothermal plumes precipitates rapidly to form fine-grained suspended Fe oxyhydroxide particles, which in clear deep-ocean waters, distant from continental sediment inputs, can be detected readily using *in situ* optical back-scatter devices.

Methods of hydrothermal plume detection

The simplest form of *in situ* plume detection is illustrated in Fig. 7, which shows the case for co-registered optical and chemical anomalies detected as the result of lowering an instrument called a CTD-rosette through a hydrothermal plume. The instrumentation on this device, the CTD, continuously measures conductivity, temperature and depth as it is lowered through the water column while the rosette component can be used to collect discrete water samples, sequentially, at a range of different depths below sea-level/above the seafloor for subsequent shore-based analyses (in this case, for dissolved Mn). Here, the instrument also collected continuous *in situ* optical back-scatter data (the red trace in Fig. 7(b)) revealing great detail about the structure within the hydrothermal plume. It was only the shore-based determination of anomalously high concentrations of dissolved Mn in the few discrete samples collected (shown in blue), however, that was able to confirm that the particle-rich waters responsible for the optical signals were, indeed, hydrothermal in nature. Furthermore, while such data show clearly that a lens of water enriched in dissolved Mn and suspended particulate material is present at this location at a water depth of 3000–3300 m, what cannot be discerned from this data set is whether those samples were taken close to, or distant from, the hydrothermal vent-source, nor in which direction that hydrothermal vent-site might lie. A much more powerful example of how to search for hydrothermal activity, then, is shown in Fig. 8. Here a deep-tow vehicle with the same capabilities as a CTD-rosette has been developed which can be towed behind a ship at depths in the range 2000–6000 m and undulated through just the bottom few hundreds of metres above the seafloor (the only depth likely to be seeded by any hydrothermal plume, see the previous section). What this allows is the construction of a series of two-dimensional slices of optical back-scatter data of the kind shown. The example in Fig. 8(b) shows, clearly, the intersection of not only the non-buoyant plume (green colours sloping 'uphill' from right to left) but, superimposed upon that, very intense particle concentrations observed when the instrument package intercepted the rising *buoyant* portion of the hydrothermal plume directly above (hence, revealing the precise location of) the source hydrothermal field.

Hydrothermal exploration on the Mid-Atlantic Ridge – Rainbow vent-field

One of the first sections of slow-spreading ridge where systematic deep-tow hydrothermal exploration was conducted was a section of the MAR immediately southwest of the Azores (Fig. 9). The results of that work were striking because much more evidence for hydrothermal activity was observed along the 200 km of ridge investigated (36–38° N) than was predicted based on spreading rate alone (German *et al.* 1996). In total, evidence was identified for at least

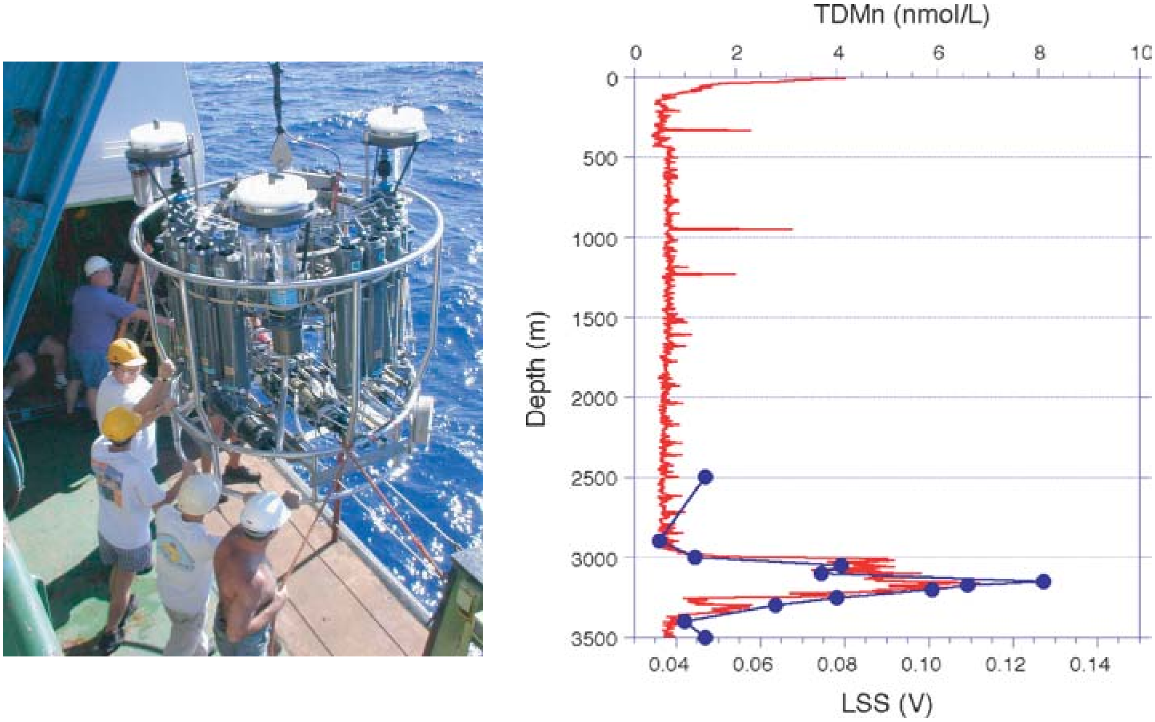

Fig. 7. (a) Picture of a conductivity–temperature–depth (CTD) rosette used for investigating vertical distributions of water column parameters from deep-ocean research vessels; (b) example of optical back-scatter (red trace) and dissolved Mn concentrations (blue) within a deep-ocean hydrothermal plume – data from Edmonds *et al.* (2003).

discrete sites of venting, the majority of which were not associated with active centres of volcanic activity but, instead, occurred close to fracture zones that off-set the spreading ridge crest: sites where hydrothermal activity had not previously been predicted to occur. Subsequent investigation on the seafloor revealed that one of these areas, the Rainbow hydrothermal field, was host to an extremely vigorous suite of high-temperature (⩾360 °C) 'black smoker' chimneys, but that these were not sited on fresh basaltic lavas. Instead, these vents were hosted at the base of a fault-scarp that exposed serpentinizing ultramafic rocks (Fouquet *et al.* 1998). Thus, at just the same time that Shock & Schulte (1998) were publishing their thermodynamic predictions for Hadean (>4 Ga) high-temperature hydrothermal systems hosted in ultramafic rocks (see earlier), a very close analogue was being located on the modern seafloor. Subsequent characterization of the Rainbow vent-fluids has revealed that these vents are largely similar to numerous other high-temperature hydrothermal systems, exhibiting a low pH (2.7–3.1) and bearing high concentrations of various trace metals together with dissolved H_2S (Douville *et al.* 2002). What was quite unlike other seafloor hydrothermal systems, however, was that the Rainbow vent-fluids also contained extremely high concentrations of methane compared with other known vent-sites ($2.5\ \mathrm{mmol\ kg^{-1}}$) and, most remarkable of all, even higher concentrations ($16\ \mathrm{mmol\ kg^{-1}}$) of free dissolved hydrogen (Charlou *et al.* 2002) – the critical 'missing component' from all previously studied bare-rock hydrothermal vent systems (see the previous section). The generation of this dissolved hydrogen can be directly attributed to the interaction between seawater and one particular mineral, olivine, in ultramafic rocks during a process known as serpentinization:

$$6[(\mathrm{Mg})_{1.5}(\mathrm{Fe})_{0.5}\mathrm{SiO_4}]+7\mathrm{H_2O}=3[\mathrm{Mg_3Si_2O_5(OH)_4}]+\mathrm{Fe_3O_4}+\mathrm{H_2} \qquad (1)$$

The apparent convergence between the modern Rainbow vent-site and the early-Earth predictions of Shock and Schulte (1998) were sufficiently striking that subsequent work has included quite detailed investigation of the organic composition of Rainbow vent-fluids. First, Holm and Charlou (2001) hypothesized that Fischer–Tropsch-type (FTT) reactions could lead the molecular hydrogen released in the Rainbow fluids to react with dissolved CO_2 at high temperatures to form organic compounds such as hydrocarbons and fatty acids. Using GC-MS analysis they revealed evidence for the synthesis of linear saturated hydrocarbons with chain lengths ranging from 16 to 29 carbon atoms (Fig. 10) and concluded that FTT reactions in ultramafic hydrothermal systems might indeed present a possible pathway for the formation of early membranes relevant to the origins of life.

Two immediate questions arise from this work. First, does the presence of *intact* organic matter within the Rainbow hydrothermal fluids necessarily represent *abiotic* organic synthesis or could it simply be the case that organic matter swept downward into the oceanic crust from overlying (life-filled) seawater does not undergo oxidative decomposition along a flow path through ultramafic rock types? Work

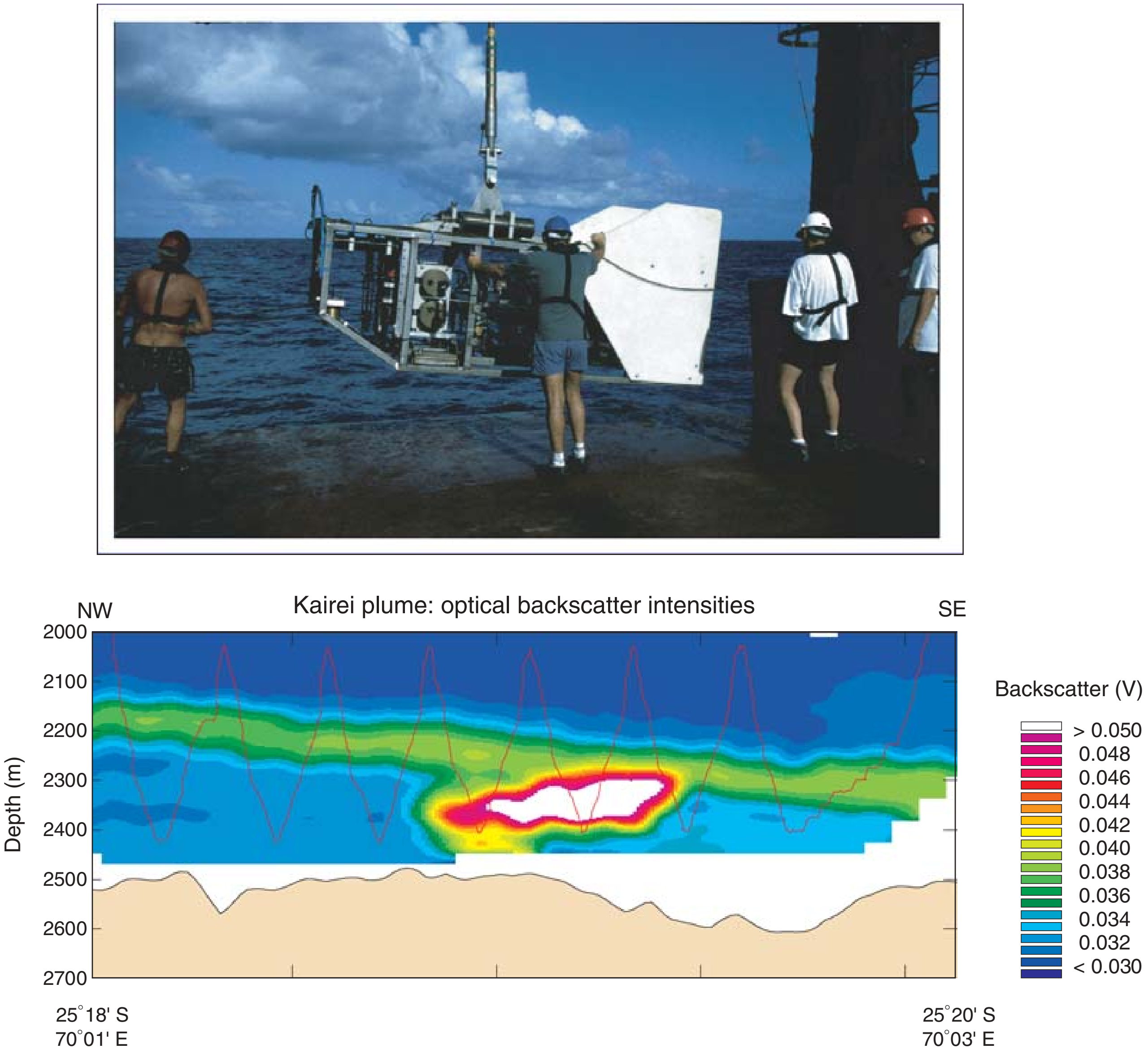

Fig. 8. (a) A picture of the BRIDGET deep-tow vehicle used for three-dimensional investigations of deep-sea hydrothermal plumes (e.g. German *et al.* 1998a); (b) an example of a two-dimensional slice of optical back-scatter data overlying the Kairei hydrothermal field, Central Indian Ridge (the thin red line shows the actual track of the undulating instrument package from which *in situ* optical back-scatter data have been contoured). Increased back scatter in hydrothermal plumes is caused by high concentrations of freshly-precipitated Fe–Mn oxyhydroxide particles, introduced into the water column at vent-sites. The SE–NW shallowing of the non-buoyant hydrothermal plume at Kairei (light and dark green) results from shoaling isopycnal (constant density) surfaces (after German 2003). Horizontal scale ~5 km.

aimed at addressing this question represents an area of active research within modern hydrothermal studies. Most recently, Simoneit *et al.* (2004) have analysed organic samples extracted from sulfide deposits and sediments (rather than vent-fluids themselves) from the Rainbow vent-site and failed to provide proof positive of abiotic organic synthesis. Instead, they concluded that the range of organic compounds they extracted (including branched and normal alkanes, polyaromatic hydrocarbons, terpenoids and fatty acids) predominantly resulted from the breakdown of biogenic matter in these samples – although they could not preclude an abiogenic origin for the methane and longer-chain alkanes reported from vent-fluids by Holm & Charlou (2001). Interestingly, broadly similar vent-fluid findings to those from Rainbow (Holm & Charlou 2001) have now been confirmed for archived vent-fluid samples from the Logatchev vent-field near 15° N on the MAR, but not for any other MAR sites (Charlou 2004). This is significant because the Logatchev site is the only other ultramafic-hosted, high-temperature vent-field yet known worldwide (Bogdanov *et al.* 1995). All other sampled MAR vent-sites are hosted in basaltic volcanism (German & Parson 1998). To investigate this matter further, therefore, leads us to a key second question: if the Rainbow system is, indeed, host to abiotic organic

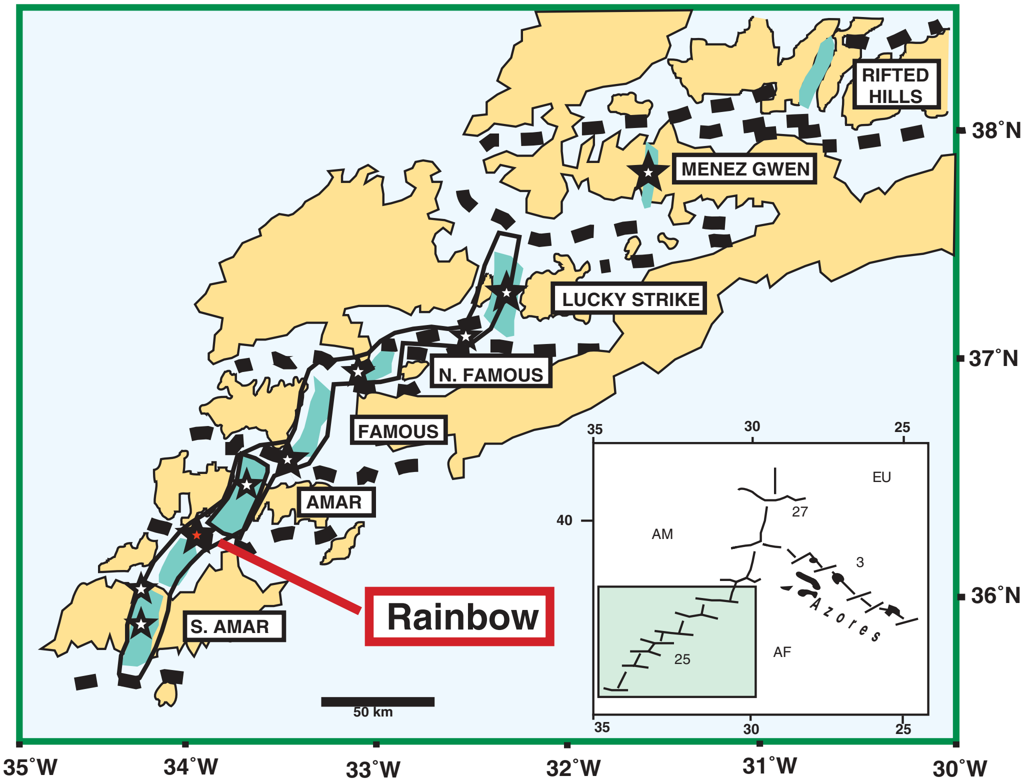

Fig. 9. A tectonic map showing locations of hydrothermal sites detected along the Mid-Atlantic Ridge, 36–38° N. Deep green shading indicates right-stepping off-setting of adjacent volcanically-active ridge segments by bounding fractures (solid dashed lines). Orange shading indicates the shallow ridge crest (<1500 m) while thin dark lines show the full extent of the survey area (after German *et al.* 1996). Stars show the locations of seven hydrothermal sites located or suspected based on an along-axis survey, in addition to the previously detected Lucky strike and Menez Gwen sites (Fouquet *et al.* 1998). The Rainbow hydrothermal field is one of four sites discovered that coincided with across-axis fracturing at segment ends away from areas of fresh/active volcanic eruption.

synthesis in a contemporary setting, how ubiquitous might such activity be along the global ridge crest?

Hydrothermal exploration along Earth's slowest ridges

Ultramafic outcrops and hydrothermal vents

It is now widely recognized (e.g. Mevel 2003) that outcropping of ultramafic rocks should only occur, typically, along the world's slower-spreading ridges such as those found in the Atlantic, Arctic and SW Indian Oceans (Fig. 5). In the Pacific Ocean, by contrast, ultramafic rocks should typically be covered in basaltic/gabbroic extrusive/intrusive rocks to a depth of greater than 6 km below the seafloor. Only in exceptional circumstances should ultramafic material be uplifted to the Pacific seabed. On slower ridges, by contrast, Cannat *et al.* (1996) have estimated that some 20% of the seafloor may be composed of serpentinized ultramafic rocks. An important question that follows immediately, therefore, is whether there might be significantly more high-temperature systems of the type already located at Rainbow and Logatchev along the world's slowest-spreading ridges. To address this question, systematic exploration was required along sections of the global ridge crest that had previously been considered those least promising for exploration based on the 'spreading-rate' hypothesis (Baker *et al.* 1996). Conveniently, however, what was clear from both the Rainbow and Logatchev sites was that those systems do still give rise to metal-rich, particle-laden plumes, just as are found above high-temperature, basalt-hosted black-smoker systems, regardless of their unusual organic geochemistry (Fig. 11). Consequently, although quite different low-temperature ultramafic systems have also now been located on the MAR (e.g. Lost City – Kelley *et al.* (2001); Saldanha – Barriga *et al.* (1998)) our earlier search strategies, biased toward detecting non-buoyant hydrothermal plumes, remain a very effective way of conducting hydrothermal exploration for all forms of high-temperature venting on slow and ultra-slow spreading ridges.

Hydrothermal activity on the SW Indian Ridge

A first focus for hydrothermal exploration along ultra-slow spreading ridges has been the SW Indian Ridge (SWIR), which extends from the Bouvet Triple Junction in the southern Atlantic to the Rodriguez Triple Junction in the southern Central Indian Ocean (Fig. 5). Two major sections of the SWIR have now been investigated for hydrothermal activity: approximately 400 km of the ridge crest between 57 and 66° E (German *et al.* 1998b) and a further section between 10 and 16°E in the southern Atlantic Ocean (Bach *et al.* 2002). From

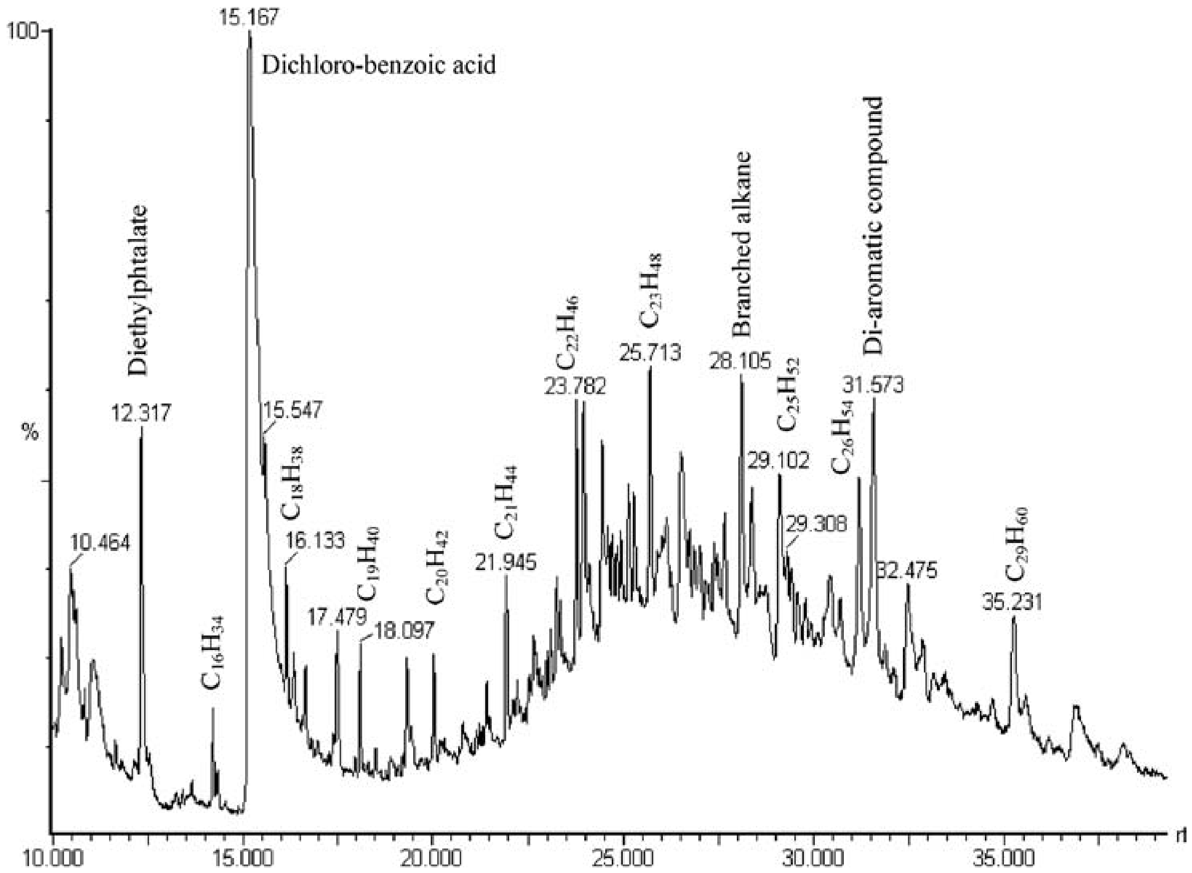

Fig. 10. GC-MS analysis of high-temperature (364 °C) vent fluids from the Rainbow hydrothermal field, 36° N, Mid-Atlantic Ridge (after Holm & Charlou 2001). The chromatogram reveals long linear hydrocarbons (C16–C29) that are present in these pristine, high-temperature, reducing, ultramafic-hosted vent-fluids. Reprinted from Earth & Planetary Science Letters, 191, N.G. Holm & J.-L. Charlou, Initial indications of abiotic formation of hydrocarbons in the Rainbow ultramafic hydrothermal system on the Mid-Atlantic Ridge, 1–8, ©(2001), with permission from Elsevier.

the eastern SWIR study, optical back-scatter anomalies revealed evidence for at least six discrete 'centres' of hydrothermal activity (German *et al.* 1998b) – at an average apparent spacing of ~65–80 km along-axis. Although none of these hydrothermal sources have yet been located on the seafloor, complementary sidescan sonar imaging of the seafloor shows that at least half of these sites are hosted in highly-faulted terrane quite decoupled from fresh seafloor volcanism – i.e. in a setting directly analogous to the Rainbow hydrothermal field (cf. German *et al.* 1996). Further west, Bach *et al.* (2002) found evidence for at least two and perhaps five separate locations of active and/or inactive hydrothermal activity within their study area. In that case, complementary collection of rock samples from the underlying seafloor revealed a very similar situation – namely that at least half of all the hydrothermal signals they obtained were associated with ultramafic, rather than basaltic, seafloor lithologies (Fig. 12).

Hydrothermal activity in the Arctic – Earth's slowest-spreading ridge-crest

Following the successes achieved during hydrothermal exploration along the remote SWIR an even more ambitious two-icebreaker expedition was conducted in 2001 to the Gakkel Ridge (Michael *et al.* 2003). This is both the World's least explored and slowest spreading ridge crest (0.6–1.3 cm yr^{-1}) and crosses the floor of the Arctic Ocean from the northernmost Atlantic toward Siberia. Although the primary focus for the 2001 cruise was petrological sampling, the opportunity was taken at each sampling site to also collect vertical profiles of overlying water column properties (Fig. 7(b)). In total, more than 1100 km of ridge axis was surveyed in this manner (Edmonds *et al.* 2003) and evidence was found for at least nine and perhaps 12 discrete hydrothermal plume sources along this section of ridge crest (Fig. 13) – a frequency directly comparable to that found along the eastern SWIR (German *et al.* 1998b). Because of the ice-covered nature of the Arctic Ocean, understanding the underlying geology of the seafloor close to these sites is problematic. Although submarine-mounted sidescan systems have been used to reveal recent active volcanism at one end of the survey area near 90° E (Edwards *et al.* 2001), it remains difficult to discern what the likely geologic setting of each site of hydrothermal activity along the Gakkel Ridge might be (Edmonds *et al.* 2003). Nor is it straightforward to develop a strategy to more accurately locate the precise source of each

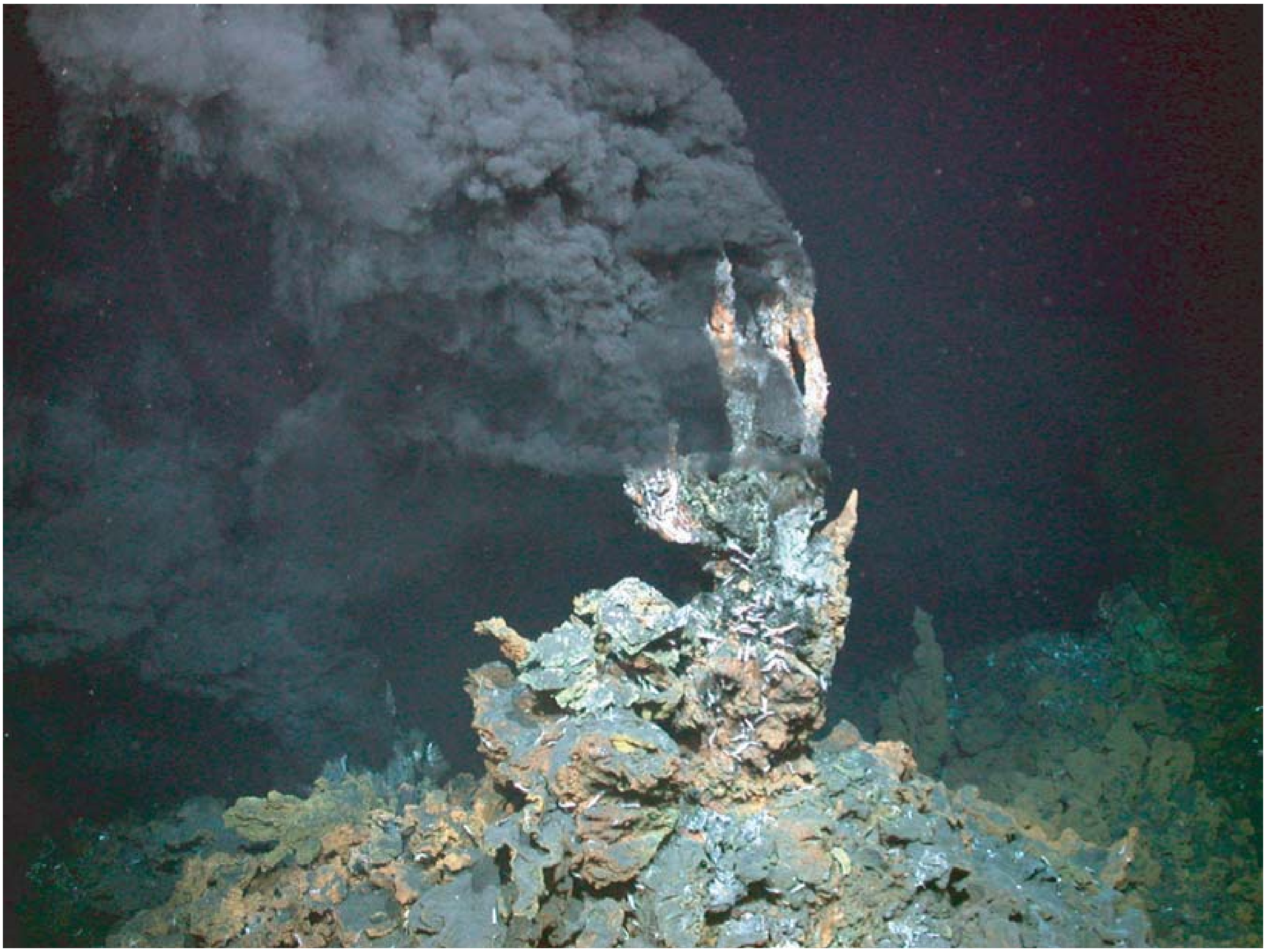

Fig 11. The Logatchev high-temperature ultramafic-hosted hydrothermal vent-field (Bogdanov *et al.* 1995) as photographed by the University of Bremen ROV, Germany (picture provided courtesy of Professor Colin Devey, IfM GEOMAR, Germany, 2003). Note that although both Logatchev and Rainbow hydrothermal vent-fluids exhibit distinctive organic geochemistries, they also give rise to the significant buoyant, metal-rich and particle-laden plumes characteristic of more typical basalt-hosted 'black-smoker' systems.

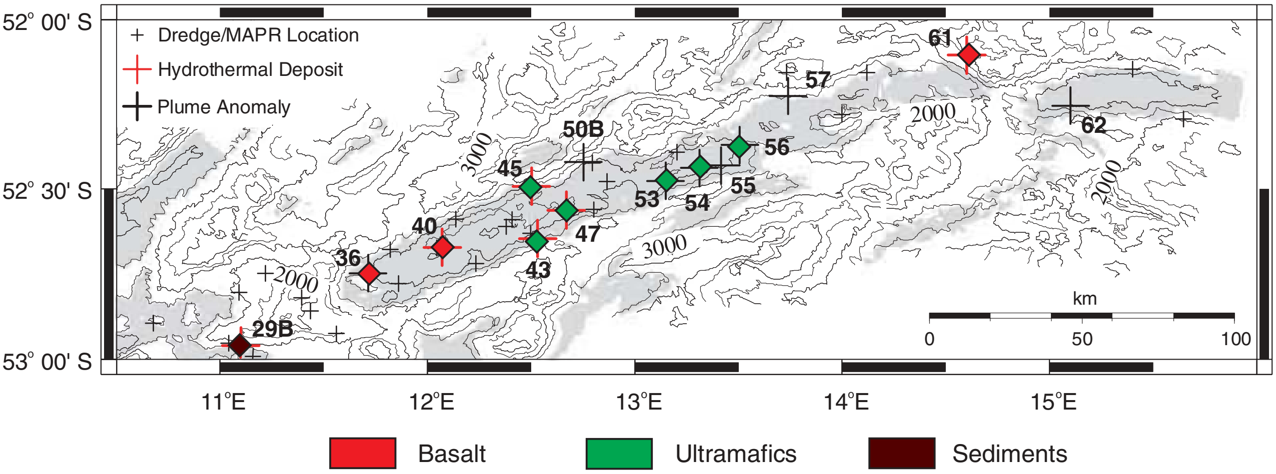

Fig. 12. Map of the SW Indian Ridge, 10–16° E showing locations of hydrothermal deposits and/or plume anomalies (grey shading indicates areas deeper than 3500 m). Colour coding is used to indicate the dominant seafloor lithology at each hydrothermal location: brown, sediment-hosted; red, MORB-hosted; green, ultramafic rocks (after Bach *et al.* 2002).

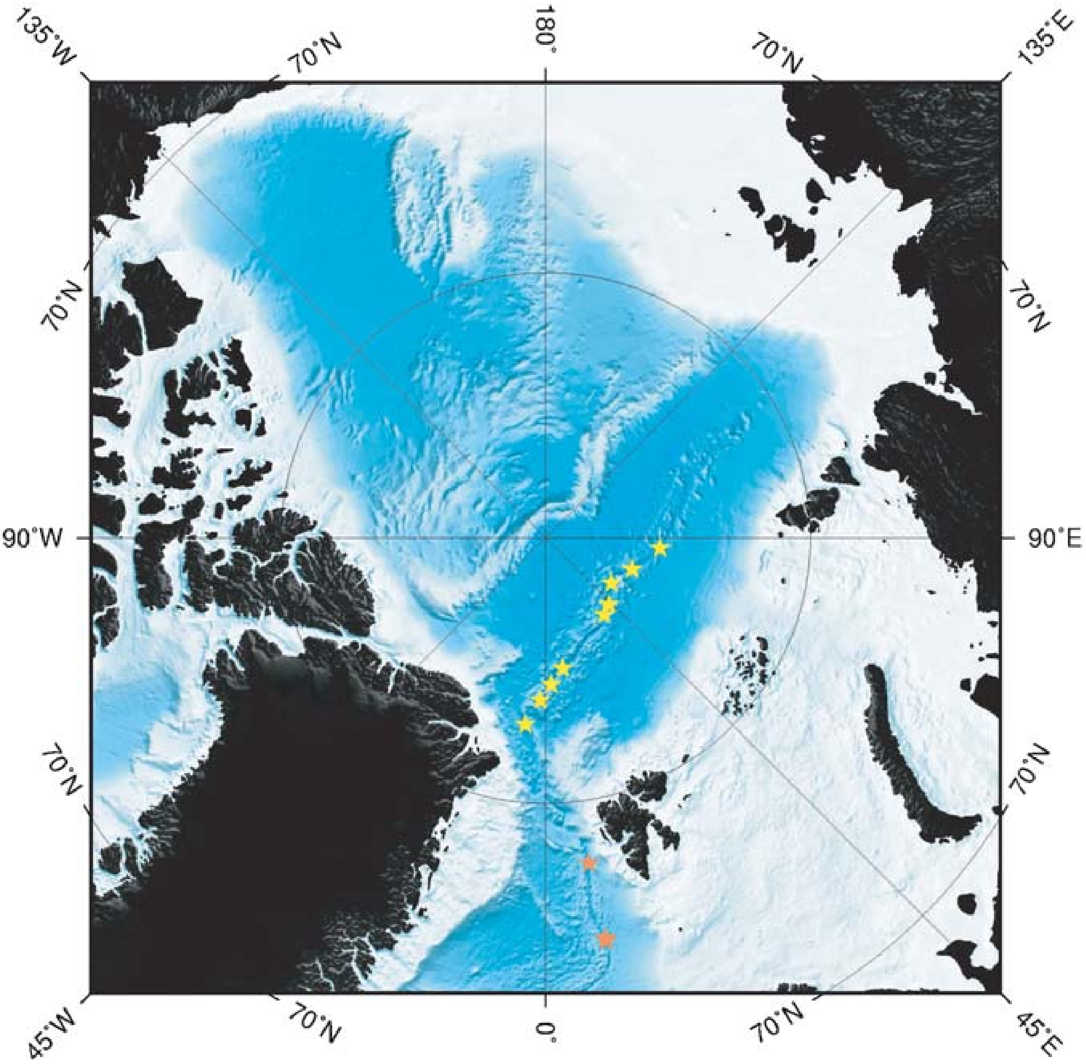

Fig. 13. Bathymetric map of the Arctic Ocean and adjacent Norwegian–Greenland Sea. Yellow stars indicate sites at which evidence for hydrothermal activity has been identified on the Gakkel Ridge (Edmonds *et al.* 2003). Orange stars indicate locations of additional hydrothermal plumes on the Knipovich Ridge (C. German, unpublished data).

vent-site on the ice-covered seafloor – clearly, our preferred method of towing instrumentation behind a research ship that is sailing at constant speed in any given direction (Fig. 8) is not an option for operations in an ice-covered ocean. Rather, new technology is required.

Hydrothermal and astrobiological exploration – a common future challenge

The challenge to oceanographers to develop a system that can explore the deep Arctic seafloor over ~1000 km distances beneath an ice-covered ocean is significant. Happily, we are no longer alone. One of the most striking results of the recently completed Galileo mission has been the emergence of a consensus that Europa, one of the four largest moons of Jupiter, is also likely to host a liquid ocean beneath an outer water-ice shell (e.g. Kivelson *et al.* 2000). Although Europa's ocean is also believed to be underlain by some rocky silicate mantle, we do not know whether active volcanism occurs at that ocean–lithosphere interface. What we do know, however, is that Io, Europa's nearest neighbour, is the most volcanically active body anywhere in our solar system (Lopez-Gautier 2000). What is also certainly the case is that wherever a mid-ocean ridge occurs, crossing Earth's ocean floor, hydrothermal circulation is known to arise – no matter how inactive the volcanism may appear to be (Baker & German 2004). It does not seem unreasonable, therefore, that future astrobiological expeditions should include, among their ambitions, a search for submarine hydrothermal activity at the bottom of Europa's oceans – or, indeed, any other such 'marine' environments as may be encountered. But how should one approach this task?

An obvious first requirement is the design of a vehicle that can move unconstrained by the overlying ice – i.e. a free swimming vehicle – and can undulate through the water column to mimic the tow-yo surveys which have previously

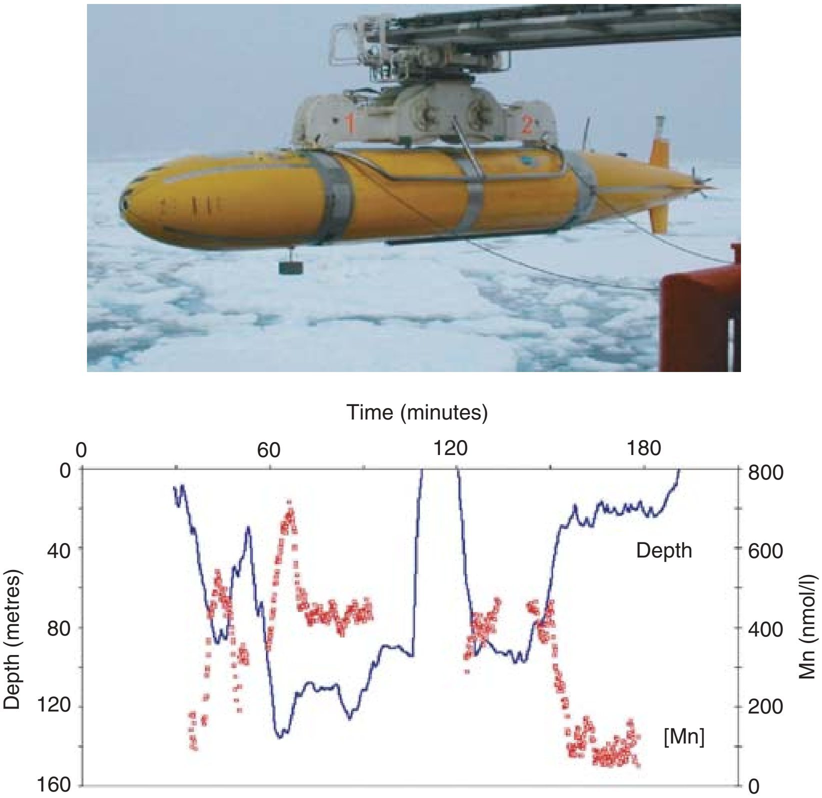

Fig. 14. (a) Southampton Oceanography Centre's *AUTOSUB* vehicle in preparation for deployment under-ice in the Southern Ocean, 2003; (b) an example of along-mission data showing *AUTOSUB* vehicle depth (continuous blue trace) and *in situ* dissolved Mn determinations (red squares) for a survey through the deep, reducing waters of upper Loch Etive, Scotland, 2001 (data from Statham *et al.* 2003).

proved so successful elsewhere (Fig. 8). A further, requirement, of course, is to equip such a vehicle with the appropriate sensors to prospect for and detect hydrothermal signals in the water column. In the UK an important first step has already been taken with the development of the long-range AUV (autonomous underwater vehicle), *AUTOSUB* (Millard *et al.* 1998). This vehicle has undertaken more than 200 missions since 1996, including first deployments beneath floating sea-ice of the Weddell Sea (Fig. 14(a)). Although other AUVs exhibit much finer-scaled manoeuvrability better suited for seafloor exploration, along with 'full-ocean depth' capability (e.g. Woods Hole Oceanographic Institution's (WHOI) *Autonomous Benthic Explorer* (*ABE*); Yoerger *et al.* (1998)) an important development with *AUTOSUB* has been the first deployment of this (or indeed *any*) AUV equipped with an *in situ* chemical sensor suitable for deep-sea hydrothermal exploration (Statham *et al.* 2003). In this first experiment of its kind (Fig. 14(b)), an *in situ* sensor was deployed on *AUTOSUB* to determine real-time concentrations of dissolved Mn enrichment within the deep-water column of a partially anoxic sea-loch on the West coast of Scotland (Loch Etive). The analyses shown here were all carried out underway and with no human intervention, as the vehicle dived to follow a path along the length of the loch bottom (*AUTOSUB* was programmed to remain 10 m off the bottom, but to surface once, mid-mission, to communicate with GPS navigation satellites) over a period of ~3 h. Although the maximum depth reached in this work was less than 200 m and the dissolved Mn concentrations measured were at least a factor of 2–10 higher than hydrothermal plume signals, we consider this an important step in the right direction. More will surely follow.

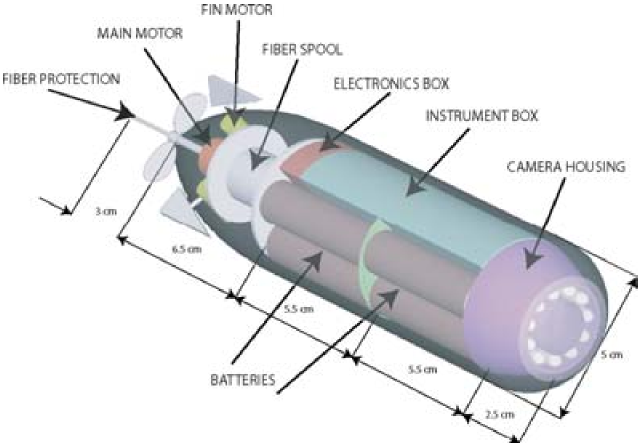

Fig. 15. Illustration of the proposed MEMS-enhanced miniature autonomous submersible explorer proposed by Bruhn *et al.* (2004) for future exploration of remote and inaccessible environments – e.g. hydrothermal vents beneath ice-covered oceans.

Indeed, plans already exist in the UK (Spring 2005) to adapt our *in situ* Mn sensor and couple it to WHOI's deep-ocean *ABE* vehicle in a bid to *autonomously* locate the first sites of hydrothermal activity to be found anywhere in the southern Atlantic Ocean – a major target for vent biogeography studies (Fig. 2; Van Dover *et al*. 2002). An even more ambitious programme includes the Southampton Oceanography Centre's contributions, together with NASA's Jet Propulsion Laboratory, USA and the Angstrom Space Technology Centre, Sweden (Bruhn *et al*. 2004) to develop a new MEMS (micro electro-mechanical systems)-enabled Miniature Autonomous Submersible Explorer. That proposed system, currently still at the design stage, would be suitable for deep-sea hydrothermal investigations (among other missions), but with the added advantage that it would be miniaturized to be deployed from both the basket of a larger manned/unmanned submersible and/or delivered into the oceans via a drilling mechanism such as that used to penetrate the ice above Lake Vostok (Bruhn *et al*. 2004). With a proposed range of some 4–10 km from its carrier vehicle, courtesy of an unspooling, single-strand, fibre-optic cable (Fig. 15), either of the proposed delivery mechanisms (beneath ice and/or through ice) might prove particularly appropriate for future hydrothermal exploration beneath the ice-covered oceans of the Arctic – or beyond!

Summary

Submarine vents on Earth's ocean floors play host to unique chemosynthetic ecosystems populated by species previously unknown to science. Because these organisms derive much of their energy from chemical redox reactions rather than photosynthesis and because hydrothermal systems are likely to have persisted throughout much of Earth history, much speculation arose, upon their first discovery, that hydrothermal vent systems might have played a significant role in the origins of life on Earth and, consequently, represent useful analogues when searching for life elsewhere in the Solar System and beyond. At one extreme, those early claims for seafloor hydrothermal systems might be rather flippantly dismissed as the direct descendants in a line of largely unconstrained speculation dating from Charles Darwin's 'warm little pond' hypothesis of more than a century ago, punctuated by Stanley Miller's now 50-year old experiments with 'primordial soup'. Certainly, the basalt-hosted systems that have dominated the first quarter of a century of modern submarine hydrothermal research appear far too oxidizing to have any promising relevance to pre-photosynthetic life.

Nevertheless, intriguing links to hydrothermal systems persist. Consensus remains that the last common ancestor for life on Earth was thermophilic or, at least, mesophilic, but exploiting redox contrasts directly akin to those found close to high-temperature hydrothermal systems. The most primitive organisms yet isolated from submarine hydrothermal fields apparently require molecular hydrogen for the energy-yielding reactions that they catalyse, yet until recently free hydrogen had only been expected to occur in high-temperature hydrothermal circulation through early-Earth's more magnesium-rich (ultramafic) komatiitic lavas.

In recent work, systematic hydrothermal exploration along slow and ultra-slow spreading ridges has revealed more hydrothermal activity than would be predicted from magmatic heat-supply alone. Typically, this 'excess' hydrothermal venting has been located away from areas of active volcanic eruption and associated, instead, with deep-penetrating faults that cut across and off-set slow-spreading ridges. An intriguing aspect of these discoveries is that the deep-seated faults that host these 'excess' vent-sites also act as mechanisms by which ultramafic rocks from the ocean crust/mantle boundary are uplifted to the seafloor. At two such locations in the Atlantic, new vent-sites have now been discovered that, although superficially similar to more typical 'black-smoker' vents, emit fluids that are rich in free hydrogen as well as exhibiting distinctive complex organic compositions. While these findings are potentially consistent with predictions for abiogenic organic synthesis in early Earth's abiotic oceans, whether the complex molecules found in these systems do indeed represent *de novo* organic synthesis remains to be proven. What is the case, however, is that such systems should not be predicted to occur anywhere along the Earth's fast-spreading mid-ocean ridges (e.g. throughout the Pacific Ocean), but may recur frequently along the length of the (still mostly unexplored) MAR and, in particular, along the SWIR and along the Gakkel Ridge beneath the ice-covered Arctic Ocean.

Preliminary investigations of the SWIR suggest that this hypothesis is broadly correct – more evidence for hydrothermal activity has been identified than is consistent with magma-supply alone and a large proportion of the signals identified (of the order of 50%) appear to be associated with ultramafic-hosted/tectonically-controlled settings. In the ice-covered Arctic Ocean, investigating the geologic setting of seafloor hydrothermal systems and collecting vent-fluid samples promises to be rather problematic. We propose this area as an excellent target for future joint oceanographic/astrobiological collaborations, to solve both extant scientific and technological challenges and to prepare for future astrobiological explorations – next stop Europa?

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