Hydrothermal Methane Venting Between 12°N and 26°N
Along the Mid-Atlantic Ridge

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INTRODUCTION

Submarine hydrothermal springs are now known to be a common phenomenon along different tectonic structures. High-temperature (>350°C) fluids issuing from these vents illustrate the effectiveness of heat and mass transfer processes associated with magmatism and subseaﬂoor convective circulation in different geodynamical environments: fast spreading ridges such as the East Pacific Rise (EPR) [von Damm et al., 1985a, b; von Damm and Bischoff, 1987; Michard et al., 1984; Campbell et al., 1987, 1988a], slow spreading ridges such as the Mid-Atlantic Ridge [Rona et al., 1986; Campbell et al., 1988b; Jean-Baptiste et al., 1991], or back arc environments such as the North Fiji [Grimaud et al., 1991] and Lau [Fouquet et al., 1990, 1991a, b; Charlo et al., 1991b] basins. Recent investigations in back arc basins and hot spot volcanoes have noted that such systems differ significantly from the better studied mid-ocean ridge hydrothermal systems [Horibe et al., 1983; Craig et al., 1987a, b; Fouquet et al., 1991a, b]. So, black smoker venting is now clearly demonstrated not to be restricted to moderate and fast spreading ridge segments [Rona et al., 1986; Baker et al., 1987a]. These springs occur over a wide range of spreading rates and are important carriers of heat and chemical species from the newly formed lithosphere into the oceans. The hydrothermal fluids injected into the ocean in the axial zone of ocean ridges are highly enriched in metallic elements [Edmond et al., 1982, 1990; Michard et al., 1984; von Damm et al., 1985a, b; von Damm and Bischoff, 1987], and in the gases helium, methane, and hydrogen [Welhan and Craig, 1979, 1983; Lilley et al., 1982a; Evans et al., 1988; Jean-Baptiste et al., 1991]. Hydrothermal venting produces a wide variety of important effects in the overlying water column, including the formation of turbulent plumes, the introduction of chemicals and biota, and the modification of deep ocean circulation and mixing patterns.

The near-field buoyant plumes originating from mixtures of high-temperature hydrothermal fluids and ambient seawater, rise to 200-400 m above the seafloor on the EPR [Charlo et al., 1991a] or on the Juan de Fuca Ridge [Baker and Massoth, 1987; Baker et al., 1987a, b; Lupton et al., 1985; Lupton, 1990]. The neutrally buoyant effluent layer forms after the buoyant plumes have attained density equilibrium and spreads laterally along isopycnal surfaces [Lupton et al., 1985, 1989] in a symmetrical or asymmetrical mode due to the morphology of the ridge axis and prevailing currents [Speer and Rona, 1989]. As the plume ages, its chemical composition changes as a result of physical and biological processes including oxidation, precipitation, dissolution, adsorption, and scavenging reactions, many of which are microbially mediated.

Because of huge enrichment factors and in spite of the dilution of hydrothermal solutions by seawater, physical (temperature, nephelometry [Nelsen et al., 1986/87]) and geochemical (helium [Craig et al., 1975; Jenkins and Clarke, 1976; Jenkins et al., 1980; Lupton, 1976; Lupton and Craig, 1981], methane [Kim, 1983], manganese [Klinkhammer et al., 1985, 1986] and radon [Kadko et al., 1990]) anomalies are produced in deep ocean waters. Simple relationships do not exist between temperature and chemical tracers, and discrepancies between temperature and chemical tracers and between chemical tracers themselves have been shown to result from a combination of various reasons [Charlo et al., 1991a]. Particularly, the
residence time of tracers in seawater can range from infinite (helium) to relatively short (Mn [Emerson et al., 1982, Cowen et al., 1986] and CH4 [Welhan and Craig, 1983; de Angelis, 1988; de Angelis et al., 1990]). Residence time of temperature anomalies is generally short due to rapid mixing. As a consequence, some tracers are only sensitive to dilution, but others are also sensitive to either oxidation, precipitation, or bacterial activity. Helium is the best stable conservative tracer for an extensive study of deep ocean mixing and circulation. Radon-222 used in conjunction with He can be used potentially to provide a clock to quantify the age of a dispersing hydrothermal plume and calculate the removal rates of other non conservative tracers such as CH4, H2, Mn, and particles [Kadko et al., 1990]. Microbial CH4 oxidation rates in buoyant and lateral plumes have been determined for a variety of hydrothermal environments [de Angelis, 1988; de Angelis et al., 1990], and prove CH4 not to be a conservative tracer. Although CH4 is thermodynamically unstable with respect to oxidation by dissolved oxygen [Ward et al., 1987, 1989] and in spite of its microbial oxidation in plumes, excess CH4 in the seawater column produced by continuous venting persists for a sufficiently long time to be used as a guide for the exploration of new hydrothermal areas. So, CH4 has proved to be a good indicator when tracking and mapping submarine hydrothermal activities in different oceans [Kim, 1983; Horibe et al., 1986; Gamo et al., 1987; Belviso et al., 1987; Charlou et al., 1987, 1988, 1991a, b; Nojiri et al., 1989; Plager et al., 1990].

In the Atlantic Ocean, CH4 has been measured, particularly in surface waters and off-axis deep waters, in order to study the exchange reactions at the seawater-atmosphere interface, to evaluate its biological production, and to establish the mechanisms of its biological or photochemical degradation in the upper layers of the ocean. From hydrothermal point of view little work had been done on the distribution of CH4 in the seawater column along the Mid-Atlantic Ridge axis. Evidence of CH4 anomalies has been shown in deepwater samples collected between 12° and 15°N during a cruise of the R/V Akademik Boris Petrov in 1985 [Charlou et al., 1988], at TAG site (26°N) during MAR/84 and MAR/88 cruises [Charlou et al., 1987, 1991c], and at MARK site (23°N) during Hydrosnake cruise on the R/V Jean Charcot, in 1988 [de Angelis, 1988]. New findings obtained during the Ridelente cruise (1988), on the RV Jean Charcot, Mid-Atlantic Ridge (MAR)/88 cruise (1988) on the NOAA ship Oceanographer and MAR/90 cruise (1990), and on the RV Atlantis II with DSV Alvin in 1990 are presented in this report. These cruises were devoted to the study of hydrothermal processes at the ridge axis. The scientific objectives were to identify the frequency of hydrothermal plumes and to delineate the hydrothermal plumes and venting sources on the seafloor between 12° and 26°N along the Mid-Atlantic Ridge (MAR) with particular attention to TAG (26°N), MARK (23°N), and 15°N areas where specific surveys were conducted to characterize the hydrothermal plume signatures. The station locations are presented in Figure 1 and Table 1.

**Sampling and Methods**

Deep seawater was collected in 8-L Niskin-type bottles mounted on a rosette in association with Neil Brown or Seabird conductivity-temperature-depth (CTD) sensors. Samples for CH4 analyses were rapidly drawn by gravity into 125-mL glass bulbs fitted with teflon vacuum valves at either end. The bulbs were filled from below and allowed to overflow vertically to about one third of their volume in order to avoid trapping air bubbles. Samples were either stored at +4°C until analyzed on board, within 4 hours after sampling to ensure efficient recovery of the dissolved methane, or poisoned with mercuric chloride or sodium azide for on shore analysis in our laboratory at IFREMER in Brest, within 2 months after sea operations. Aboard ship, CH4 equipment was set up in a portable clean air-conditioned van, permitting CH4 analysis every 15 min, 24 hours a day.

The trapping method [Swinnerton and Linnenbom, 1967; Scranston and Brewer, 1977; Lilley et al., 1983] (which allowed us to work on smaller volumes (100-250 mL)) was chosen in this study. Dissolved gases were stripped from the seawater and were concentrated at -80°C on two 3/16 inch o.d. stainless steel traps which contained activated alumina for trapping C2-C4 hydrocarbons and activated charcoal for trapping CH4 and CO2, respectively. For this study, only CH4 was analyzed. By raising the trap temperature, the CH4 was desorbed from activated charcoal and injected into the chromatographic column placed in the 100°C heated oven of a DELSI Instrument chromatograph equipped with a flame ionization detector. Peaks were recorded and integrated on an ICR 1 B Shimadzu integrator. For calibration of the gas chromatograph, Air Liquid/Alflagaz CH4 standards (2 ppmv +/-2% and 10 ppmv +/-2% in pure helium) were injected through calibrated loops to the detector at appropriate time intervals. Known amounts of CH4 injected into the stripping/trapping line, following the same steps as those used in water sample analysis permitted a good standardization. Blanks were measured between samples. A 3% standard deviation was obtained for 2 nmol/kg surface samples. The limit of detection was 0.02 nmol CH4 per kilogram of seawater. Taking into account the precision of the calibration, blanks correction, and reproducibility, the precision was +/-3% within a CH4 concentration range of 0.22-18 nmol/kg.

**CH4 ANOMALIES IN DEEP WATER AT SPREADING AXES**

In oceanic regions unaffected by hydrothermal inputs, deep waters are CH4 undersaturated due to in situ consumption [Scarnston and Brewer, 1978], and CH4 concentrations decrease with depth to respectively backgrounds of about 0.18 nmol/kg in the Pacific and 0.36 nmol/kg in the Atlantic [Lamontagne et al., 1973, 1974; Scarnston and Lamontagne, 1974; Kim, 1983; Charlou et al., 1987, 1988, 1991a, b] between 1500 m depth and the seafloor.

In hydrothermal systems, CH4 is enriched and may be derived from multiple carbon sources, particularly in geologically complex hydrothermal systems: thermocatalysis of organic matter in sediments [Welhan and Lupton, 1987; Welhan, 1988; Welhan et al., 1988], biogenic processes including bacterial production at low temperature [Lilley et al., 1983; Baross et al., 1982; Schoell, 1988], outgassing of juvenile carbon as CH4 from the mantle via-high temperature hydrothermal systems [Gold and Soter, 1982; Welhan and Craig, 1982, 1983], and abiogenic seawater-rock interaction involving CH4 generation through reactions at high temperature (>300-400°C) (such as the Fischer-Tropsch synthesis) in which CO2, H2, H2O, and other hydrocarbon species may participate [Welhan and Craig, 1982, 1983; Welhan, 1988a]. Seafloor hydrothermal discharges exhibit a wide range of CH4 contents (Table 3) which can be explained in terms of seawater-rock interaction in different geological contexts.

CH4-enriched plumes were first found along the axes of
Fig. 1. Regional map of the Mid-Atlantic Ridge between 12°N and 26°N, showing locations of Fifteen Twenty Fracture Zone (FTZ), MARK, and TAG areas. Solid circles mark the CTD vertical profiles conducted in the axial area during *Akademik Boris Petrov* (1985) (stations 36, 38, 39) and *Ridelente* (1988) (stations 4 to 27) cruises. Squares mark known venting sites TAG (26°N) and MARK (23°N) studied during *Atlantis III Alvin* cruise in 1990. The eastern intersection of the rift axis with the 15°-20°N FTZ where specific and intense hydrographic surveys were conducted during *Ridelente* (1988) and MAR/88 (1988) cruises is also marked. The precise latitudes and longitudes of stations are shown in Table 1.

medium to fast spreading centers, such as the Galapagos Spreading center at 86°W [Lilley et al., 1983], along the East Pacific Rise at 20°S and 21°N [Kim, 1983], 13°N [Charlou et al., 1991a], in the Guaymas Basin, on the Gorda [Baker et al., 1987a], and Endeavour [Rosenberg, 1988; Winn et al., 1986] ridges, and the Axial seamount on the Juan de Fuca Ridge [Butterfield et al., 1990]. Large plumes of CH₄-enriched water have been detected in back arc basins: the North Fiji basin [Auzende et al., 1986; Sedwick et al., 1990], Mariana [Horibe et al., 1986] and Okinawa [Kimura et al., 1988] troughs, the Lau basin [Charlou et al., 1991b], and other basins in the southwest Pacific [Craig et al., 1987b; Belviso et al., 1987], or in other locations such as the Red Sea [Blanc et al., 1990], the Gulf of Aden [Jean-Baptiste et al., 1990] or the Indian Ocean [Pluinger et al., 1990]. CH₄ plumes are also clearly identified in the summit crater of the Loihi seamount [Gamo et al., 1987] at the present site of the Hawaiian hot spot, thus establishing the widespread existence of off-ridge hydrothermal vents in the ocean. Steady state emanations of hydrothermal vent fluid along ridges such as the East Pacific Rise give clearly defined CH₄ plumes rising 100-300 m above the seafloor. Recently however, a quite different type of hydrothermal plume created by a brief but massive release of high-temperature hydrothermal fluids ("megaplume") was discovered on the Juan de Fuca Ridge [Baker et al., 1987b] and above the North Fiji Basin spreading axis [Nojiri et al., 1989]. More recently, reports of CH₄ anomalies in the seawater column above some hydrothermal fields along the MAR have been published (12° to 15°N [Charlou et al., 1988, 1991c], 23°N [Jean- Baptiste et al., 1991], 26°N [Charlou et al., 1987, 1991c].

**RESULTS**

**TAG Field (26°N)**

The TAG site (26°N) is located on a 10-km segment of the east wall of the rift valley on the MAR about 275 km north of the Kane Fracture Zone [Rona et al., 1984, 1986]. A low-temperature hydrothermal area was delineated between 2400 m and 3100 m on this east wall through temperature [Rona et al., 1984] and He anomalies [Jenkins et al., 1980]. The presently active black smoker system occurs at the juncture between the rift valley floor and the east wall at a depth of 3620-3700 m at 26° 08'N, 44° 49'W [Rona et al., 1986; Thompson et al., 1988].

The hydrothermal fluid samples collected by the DSV *Alvin* at the TAG site in January 1990 confirmed the first submersible observations in 1986 (Table 2a and Figure 2a [Campbell et al., 1988b]). Despite the much greater depth of these vents (3700 m) relative to the EPR depths at 13° or 21°N (2500 m) they displayed similar mineral composition and an exit temperature surprisingly similar to those observed on the EPR [Campbell et al., 1988a]. The nonsulfide-forming major and minor element
TABLE 1. Location of CTD/Casts Stations Between 12°N and 23°N Conducted During Akademik Boris Petrov (1985), Ridelente (1988), and MAR/88 Cruises Showing Maxima CH₄ Concentrations and Corresponding Water Depths

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Bottom Depth, m</th>
<th>Sample Depth, m</th>
<th>CH₄ maximum, nmol/kg</th>
<th>Geological Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-HY-36</td>
<td>12°24'</td>
<td>44°05'</td>
<td>4800</td>
<td>3541</td>
<td>1,85</td>
<td>Between TFZ and UFZ</td>
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<tr>
<td>AK-HY-38</td>
<td>13°47'</td>
<td>44°59'</td>
<td>3900</td>
<td>2500</td>
<td>0,77</td>
<td>Between 15°FZ and TFZ</td>
</tr>
<tr>
<td>AK-HY-39</td>
<td>14°05'</td>
<td>45°01'</td>
<td>3000</td>
<td>2715</td>
<td>1,31</td>
<td>Between 15°FZ and TFZ</td>
</tr>
<tr>
<td>RD-HY-01</td>
<td>15°05.1'</td>
<td>49°22.15'</td>
<td>3030</td>
<td>2000</td>
<td>1,13</td>
<td>off axis station</td>
</tr>
<tr>
<td>RD-HY-02</td>
<td>14°46.05'</td>
<td>48°09.57'</td>
<td>3260</td>
<td>2300</td>
<td>0,45</td>
<td>off axis station</td>
</tr>
<tr>
<td>RD-HY-03</td>
<td>14°35.63'</td>
<td>46°07.94'</td>
<td>3906</td>
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<td>0,50</td>
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<tr>
<td>RD-HY-04</td>
<td>14°55.66'</td>
<td>46°55.20'</td>
<td>4005</td>
<td>2897</td>
<td>3,42</td>
<td>Eastern Ridge axis/15°20 FZ Intersection</td>
</tr>
<tr>
<td>RD-HY-05</td>
<td>15°35.97'</td>
<td>46°33.51'</td>
<td>3994</td>
<td>3101</td>
<td>2,75</td>
<td>Western Ridge axis/15°20 FZ Intersection</td>
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<td>RD-HY-06</td>
<td>15°48.51'</td>
<td>46°33.66'</td>
<td>3403</td>
<td>3250</td>
<td>3,74</td>
<td>Western Ridge axis/15°20 FZ Intersection</td>
</tr>
<tr>
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<td>16°08.12'</td>
<td>46°40.33'</td>
<td>4017</td>
<td>3589</td>
<td>1,53</td>
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</tr>
<tr>
<td>RD-HY-08</td>
<td>15°44.89'</td>
<td>46°32.98'</td>
<td>3630</td>
<td>3203</td>
<td>2,16</td>
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</tr>
<tr>
<td>RD-HY-09</td>
<td>16°01.26'</td>
<td>48°06.56'</td>
<td>4837</td>
<td>2800-4827</td>
<td>0,36</td>
<td>Royal Through</td>
</tr>
<tr>
<td>RD-HY-10</td>
<td>16°37.42'</td>
<td>46°30.35'</td>
<td>4230</td>
<td>2498</td>
<td>1,85</td>
<td></td>
</tr>
<tr>
<td>RD-HY-11</td>
<td>16°91.68'</td>
<td>46°27.96'</td>
<td>4724</td>
<td>3400</td>
<td>1,26</td>
<td></td>
</tr>
<tr>
<td>RD-HY-12</td>
<td>17°08.99'</td>
<td>46°29.62'</td>
<td>3905</td>
<td>3200-3800</td>
<td>0,99</td>
<td></td>
</tr>
<tr>
<td>RD-HY-13</td>
<td>17°18.79'</td>
<td>46°26.92'</td>
<td>3655</td>
<td>3496-3655</td>
<td>0,99</td>
<td></td>
</tr>
<tr>
<td>RD-HY-14</td>
<td>17°29.77'</td>
<td>46°27.44'</td>
<td>4300</td>
<td>3300-3500</td>
<td>0,99</td>
<td></td>
</tr>
<tr>
<td>RD-HY-15</td>
<td>18°13.04'</td>
<td>46°25.79'</td>
<td>3847</td>
<td>900-2500</td>
<td>0,27</td>
<td>30 miles east of Ridge axis</td>
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<tr>
<td>RD-HY-16</td>
<td>18°14.44'</td>
<td>46°39.87'</td>
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<td>3200-3600</td>
<td>0,77</td>
<td></td>
</tr>
<tr>
<td>RD-HY-17</td>
<td>18°39.53'</td>
<td>46°17.53'</td>
<td>4023</td>
<td>3600</td>
<td>0,90</td>
<td></td>
</tr>
<tr>
<td>RD-HY-18</td>
<td>18°48.30'</td>
<td>46°14.75'</td>
<td>3823</td>
<td>3800</td>
<td>0,77</td>
<td></td>
</tr>
<tr>
<td>RD-HY-19</td>
<td>19°06.81'</td>
<td>46°01.86'</td>
<td>3640</td>
<td>2600-3600</td>
<td>0,45</td>
<td></td>
</tr>
<tr>
<td>RD-HY-20</td>
<td>19°35.50'</td>
<td>45°56.20'</td>
<td>3450</td>
<td>2900</td>
<td>0,72</td>
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</tr>
<tr>
<td>RD-HY-21</td>
<td>19°58.54'</td>
<td>45°43.22'</td>
<td>4510</td>
<td>2000-4500</td>
<td>0,32</td>
<td></td>
</tr>
<tr>
<td>RD-HY-22</td>
<td>20°21.53'</td>
<td>45°37.35'</td>
<td>3485</td>
<td>2594</td>
<td>0,77</td>
<td></td>
</tr>
<tr>
<td>RD-HY-23</td>
<td>21°51.35'</td>
<td>45°13.09'</td>
<td>3070</td>
<td>2848</td>
<td>0,90</td>
<td></td>
</tr>
<tr>
<td>RD-HY-24</td>
<td>23°13.52'</td>
<td>44°54.01'</td>
<td>4075</td>
<td>3702</td>
<td>2,34</td>
<td>South MARK site</td>
</tr>
<tr>
<td>RD-HY-25</td>
<td>23°24.60'</td>
<td>45°00.00'</td>
<td>4350</td>
<td>3500-3900</td>
<td>0,90</td>
<td>North MARK site</td>
</tr>
<tr>
<td>RD-HY-26</td>
<td>23°39.55'</td>
<td>45°10.05'</td>
<td>4300</td>
<td>2500-4300</td>
<td>0,32</td>
<td>KANE FZ</td>
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<tr>
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<td>23°21.54'</td>
<td>44°56.99'</td>
<td>3680</td>
<td>3392</td>
<td>1,26</td>
<td>500 m south MARK site</td>
</tr>
</tbody>
</table>

**Akademik Boris Petrov Cruise (1985)**

**Ridelente Cruise (1988)**

**MAR/88 Cruise (NOAA-MAR Program) (1988)**

<table>
<thead>
<tr>
<th>Cast</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Bottom Depth, m</th>
<th>Sample Depth, m</th>
<th>CH₄ maximum, nmol/kg</th>
<th>Geological Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast 01</td>
<td>26°09.1'</td>
<td>44°50.5'</td>
<td>3615</td>
<td>2000</td>
<td>0,59</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 02</td>
<td>26°08.4'</td>
<td>44°49.6'</td>
<td>3652</td>
<td>2996</td>
<td>0,68</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 03</td>
<td>26°08.1'</td>
<td>44°49.7'</td>
<td>3387</td>
<td>3305</td>
<td>8,33</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 04</td>
<td>26°08.3'</td>
<td>44°49.8'</td>
<td>3732</td>
<td>3438</td>
<td>9,05</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 06</td>
<td>26°09.9'</td>
<td>44°48.8'</td>
<td>3480</td>
<td>3412</td>
<td>9,45</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 07</td>
<td>26°08.1'</td>
<td>44°49.4'</td>
<td>3843</td>
<td>3263</td>
<td>9,00</td>
<td>TAG area</td>
</tr>
<tr>
<td>Cast 08</td>
<td>26°07.8'</td>
<td>44°50.8'</td>
<td>3757</td>
<td>2502</td>
<td>2,70</td>
<td>lower east wall</td>
</tr>
<tr>
<td>Cast 09</td>
<td>26°07.3'</td>
<td>44°50.9'</td>
<td>2964</td>
<td>2900</td>
<td>2,66</td>
<td>base of east wall</td>
</tr>
<tr>
<td>Cast 10</td>
<td>14°56.3'</td>
<td>44°53.9'</td>
<td>2923</td>
<td>2603</td>
<td>3,56</td>
<td>lower east wall</td>
</tr>
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<td>Cast 11</td>
<td>14°55.0'</td>
<td>44°54.1'</td>
<td>3554</td>
<td>2960</td>
<td>4,77</td>
<td>lower east wall</td>
</tr>
<tr>
<td>Cast 12</td>
<td>14°54.1'</td>
<td>44°54.6'</td>
<td>3550</td>
<td>2997</td>
<td>17,78</td>
<td>east margin to center of dome</td>
</tr>
<tr>
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<td>15°06.5'</td>
<td>44°55.2'</td>
<td>3475</td>
<td>2803</td>
<td>15,62</td>
<td>east margin to center of dome</td>
</tr>
<tr>
<td>Cast 15</td>
<td>15°05.7'</td>
<td>44°57.0'</td>
<td>3029</td>
<td>2591</td>
<td>2,12</td>
<td>north margin to center of dome</td>
</tr>
<tr>
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<td>15°06.7'</td>
<td>44°56.9'</td>
<td>2773</td>
<td>2500</td>
<td>5,27</td>
<td>south to north transect on east wall</td>
</tr>
<tr>
<td>Cast 17</td>
<td>14°56.1'</td>
<td>44°51.5'</td>
<td>14°54.0'</td>
<td>44°53.4'</td>
<td>2798</td>
<td>east to west transect from east wall</td>
</tr>
</tbody>
</table>
TABLE 2a. MAR/90 (Atlantis II/Alvin Cruise): CH₄ in the Neutrally Buoyant Plume Above TAG

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>Bottle</th>
<th>Si(OH)₄, μmol/kg</th>
<th>Mn, nmol/kg</th>
<th>CH₄, nmol/kg</th>
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<tr>
<td>3490</td>
<td>3</td>
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<td>3.5</td>
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<td>4.2</td>
<td>3.5</td>
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<td>(leaks)</td>
<td>6</td>
<td>(5)</td>
<td>(1.5)</td>
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<td>2.5</td>
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<tr>
<td>3200</td>
<td>8</td>
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</tr>
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<tr>
<td>3098</td>
<td>10</td>
<td>3.5</td>
<td>0.2</td>
<td>0.63</td>
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</table>

Bottom depth of 3650 m.

Table 2b. MAR/90 (Atlantis II/Alvin Cruise): CH₄ in Buoyant Plumes Above TAG and MARK Sites

<table>
<thead>
<tr>
<th>Dive</th>
<th>Bottle</th>
<th>Si(OH)₄, μmol/kg</th>
<th>Mn, nmol/kg</th>
<th>Li, μmol/kg</th>
<th>CH₄, nmol/kg</th>
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<tr>
<td>TAG Buoyant Plume</td>
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<td></td>
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<tr>
<td>2182</td>
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<td>1550</td>
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<td>2182</td>
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<td>2182</td>
<td>9</td>
<td>52</td>
<td>490</td>
<td>25.5</td>
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<td>2182</td>
<td>11</td>
<td>70</td>
<td>930</td>
<td>26.5</td>
<td>98.1</td>
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<td>1</td>
<td>63</td>
<td>820</td>
<td>26.4</td>
<td>64.4</td>
</tr>
<tr>
<td>2185</td>
<td>9</td>
<td>223</td>
<td>7000</td>
<td>28.6</td>
<td>672.7</td>
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<td>MARK Buoyant Plume</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>2192</td>
<td>1</td>
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<td>740</td>
<td>27.8</td>
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</tr>
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<td>2192</td>
<td>9</td>
<td>219</td>
<td>3850</td>
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<td>326.8</td>
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<tr>
<td>2192</td>
<td>12</td>
<td>151</td>
<td>2240</td>
<td>29.2</td>
<td>300</td>
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</tbody>
</table>

TAG bottom depth, 3650m; MARK bottom depth, 3450m. All samples are taken between 10 and 40m above vents.

TABLE 2c. MAR/90 (Atlantis II/Alvin Cruise): CH₄ in Hot Fluids From TAG and MARK Sites

<table>
<thead>
<tr>
<th>Dive</th>
<th>Bottle</th>
<th>Temperature, °C</th>
<th>Mg, mmol/kg</th>
<th>pH</th>
<th>Si(OH)₄, mmol/kg</th>
<th>H₂S, mmol/kg</th>
<th>CH₄*, nmol/kg</th>
<th>CH₄**, nmol/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAG Vents</td>
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<td></td>
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<tr>
<td>B.S.2179</td>
<td>5C</td>
<td>364</td>
<td>2.9</td>
<td>3.29</td>
<td>19.75</td>
<td>0.5</td>
<td>143.1</td>
<td>150</td>
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<tr>
<td>B.S.2186</td>
<td>3C</td>
<td>360</td>
<td>3.4</td>
<td>3.46</td>
<td>17.90</td>
<td>0.5</td>
<td>142.2</td>
<td>151</td>
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<td>300</td>
<td>14.4</td>
<td>3.05</td>
<td>13.70</td>
<td>0.1</td>
<td>107.5</td>
<td>146</td>
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<td>W.S.2191</td>
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<td>300</td>
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<td>4.79</td>
<td>6.50</td>
<td>0.1</td>
<td>49</td>
<td>143</td>
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<tr>
<td>MARK Vents</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B.S.2192</td>
<td>2C</td>
<td>337</td>
<td>45.7</td>
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<td>1.60</td>
<td>0.0</td>
<td>6.7</td>
<td>48.7</td>
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<tr>
<td>B.S.2192</td>
<td>7C</td>
<td>92</td>
<td>40.6</td>
<td>0.6</td>
<td>3.65</td>
<td>0.1</td>
<td>14</td>
<td>59.4</td>
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<tr>
<td>B.S.2194</td>
<td>4C</td>
<td>352</td>
<td>27.5</td>
<td>0.5</td>
<td>8.80</td>
<td>0.5</td>
<td>22.5</td>
<td>46.4</td>
</tr>
</tbody>
</table>

Bottom water samples: Si, 35.5 μmol/kg; Mn, 0.20 nmol/kg; Mg, 53 nmol/kg; CH₄, 0.40 nmol/kg.

* concentrations measured in samples,
** End-members calculated by extrapolation for individual vents to zero magnesium. Chemical data, except CH₄, are from A. Campbell (personal communication, 1990).

Fig. 2. MAR/90 (Atlantis II/Alvin cruise). (a) CH₄ end-members calculated for a zero Mg concentration in TAG (q) (150 μmol/kg) and MARK (n) (48 μmol/kg) fluids. CH₄ endmember (62 μmol/kg) obtained in fluids sampled during the French Hydrosnake (1988) cruise above MARK (D) are presented for comparison. (b) CH₄/Si correlations found in the same TAG and MARK vent fluids.
Total condensable gas was extracted and collected in copper al, found during the French Hydrosnake cruise in 1988. TAG and MARK samples were collected differently from those in tubes, before He and CH₄ analysis on shore. CH₄ and He gas (337°-352°C) vent (Table et al, 1990]. The CH₄ end-member calculated in high temperature significantly different from those of the 1986 expedition [Edmond ln, 1991], The 1990 [Jean-Baptiste et al., Ocean background values (Figure 2a) corresponding to 10⁶ times higher than deep Atlantic mixing line calculation gives a CH₄ end-member of 62 nmol/kg. We confirmed the mineral composition previously documented one believed to have its origin on the rift valley's east wall [Nelsen and Forde, 1991].

MARK Site (Snakepit, 23° N) (Figure 3)

The MARK (or Snakepit) site at 23°22.08'N-44°57.00'W is the second major high temperature hydrothermal area discovered to date on the Mid-Atlantic Ridge; It is located in the median valley about 25 km south of the Kane Fracture Zone (Figure 3). The fluids collected at Snakepit by the DSV Alvin in January 1990 also showed mineral composition and temperatures not significantly different from those of the 1986 expedition [Edmond et al., 1990]. The CH₄ end-member calculated in high temperature (337°-352°C) vent (Table 2c) samples showed values of 46 to 49 nmol/kg. We confirmed the mineral composition previously found during the French Hydrosnake cruise in 1988 [Donval et al., 1989]. A complete gas extraction was performed on board. Total condensable gas was extracted and collected in copper tubes, before He and CH₄ analysis on shore. CH₄ and He gas concentrations are positively correlated with Mg contents. A mixing line calculation gives a CH₄ end-member of 62 nmol/kg (Figure 2a) corresponding to 10⁶ times higher than deep Atlantic Ocean background values [Jean-Baptiste et al., 1991]. The 1990 TAG and MARK samples were collected differently from those in 1988 using glass bulbs, and CH₄ was analyzed by the stripping/trapping method on shore. CH₄ extracted from the samples was calculated to be more than 95% recovery. Even if we allowed for a possible loss of gas during the 1990 sampling, the concordance between the 1988 and 1990 CH₄ data in the MARK samples indicates that in each case the gas sampling operation was well conducted and the loss of gas was considered negligible in calculations. We cannot affirm there is a CH₄ decrease between 1988 and 1990 at the MARK site; however, CH₄ concentration in the TAG fluids is surely 3 times higher than in the MARK fluids. CH₄ concentrations found in Snakepit fluids are uniform and of the same order of magnitude as those found in the 21°N rift valley (Table 2b). During the Ridelente cruise in 1988, four CTD/casts were conducted in the MARK area (Figure 4). A typical CH₄ reference profile is found at RD-HY-26 located at 23°39.55N in the Kane FZ. RD-HY-25, just north of the MARK site, shows a CH₄ plume (0.89 nmol/kg) extending into the 3400-4400 m layer. RD-HY-27 and RD-HY-24 located 500 m and 4 km south of the MARK site in the ridge axis each show CH₄ anomalies of 1.34 and 2.32 nmol/kg both centered around 3400-3700 m depth, demonstrating the plume is entrained to the south and showing that a more intense discharge may be found south of the previously known MARK site.

Hydrothermal Activity at the Eastern Ridge Axis/15°20'N FZ Intersection (Figure 5)

Morphotectonic features at the eastern intersection of the rift valley with the Fifteen-Twenty Fracture Zone are described by Rona et al., (1992). In this area, the rift valley floor is 13 km wide...
hydrothermal venting was confirmed at TAG, based on an
compare hydrothermal plumes found above the TAG field (26°N)
depth, thus confirming the previous manganese and helium data.

eastern and western ridge axis/15°20' N FZ intersections 
Charlou

CH4 profile near the background.

RD-HY-24
RD-HY-25
RD-HY-25
RD-HY-26
RD-HY-26
RD-HY-27

Fig. 4. CH4 concentration versus depth at stations RD-H-24, 25, 26 and 27
during the Ridelente cruise (1988), and around MARK area
(23°22.08'N-44°57.00'W). RD-Hy-26 conducted in Kane FZ. shows a
CH4 profile near the background.

at the 3800 m isobath. Dome-shaped features occur on opposite
sides of the rift valley at the base of the west and east wall (Figure
5). The inside-corner high at the eastern intersection of the
15°20'N FZ is a structure similar to those studied elsewhere at
slow spreading ridge axes/fracture zone intersections (such as at
the Kane, Vema, Oceanogapher, or Atlantis II fracture zones).
The recovery of serpentinized ultramafic rocks associated with
hydrothermal activity at the ridge axis/15°20'N FZ intersection
was reported by Rona et al. [1987, 1988] and Bougault et al.
[1990ab, this issue].

During the Ridelente cruise in 1988, CH4 anomalies reaching
2.7-3.6 nmol/kg were observed in the rift valley close to the
eastern and western ridge axis/15°20' N FZ intersections [Charlou
et al., 1991c]. A CH4 profile (RD-HY-04) positioned at
14°55.66'N-44°55.20'W in the rift axis (water depth of 4005 m)
(Figures 5 and 6) revealed an anomaly extending between 3500
and 2500 m depth with a maximum of 3.6 nmol/kg at 2900 m
depth, thus confirming the previous manganese and helium data.

As a part of the 1988 NOAA Mid-Atlantic Ridge Program
[Rona et al., 1988], CH4 and Mn tracers were used to identify and
compare hydrothermal plumes found above the TAG field (26°N)
and in the rift valley at 15°N close to the eastern ridge
axis/15°20'N FZ intersection (Figures 5 and 6). Active
hydrothermal venting was confirmed at TAG, based on an
elevated concentration of TDM (up to 30 nmol/kg), high CH4
concentration (up to 8.9 nmol/kg) and elevated nephelometry
signals. Plumes of a different composition were identified at 15°N
with surprisingly high CH4 concentration (up to 17.6 nmol/kg),
associated with low total dissolved Mn concentration (TDM < 1
nmol/kg) and no significant nephelometry signal [Charlou et al.,
1991c]. In the rift valley, CH4 increases from near ambient values
over the center of the rift valley to moderately higher values over
the east wall (Figure 6). The maximum anomalies occur at water
depths of between 2800 and 2900 m, consistent with a source in
the east wall. A CTD tow ascending a dome (Figure 5) centered
near the axis of the rift valley at 15°05'N-44°55'W, from
the eastern margin (water depth of 3400 m) to the dome top (water
depth of 2500 m) exhibited an abrupt increase in CH4 (up to 17.6
nmol/kg) associated with a small TDM anomaly (<1.5 nmol/kg)
over the eastern margin and a broader increase in CH4 (up to 6.7
nmol/kg) over the center. Relatively high CH4 concentrations
and very low TDM concentrations are present in all samples collected
between 5 and 50 m over the center of the dome. Suspended
particulate matter measured by optical scattering in the water
column (nephelometry) and by filtering water samples remained
near background levels (10 μg/L) at the stations sampled in the
rift valley and over the dome [Charlou et al., 1991c; Rona et al.,
1992]. The 15°N plumes rising from the mount at 2500 and 2950
m exhibit large enrichment of CH4 with lesser TDM enrichment.
The CH4 anomalies are clearly defined around 2500 and 3000 m
depths, giving a typical bimodal shape for CH4 profiles in this
area. This characteristic was never observed on CH4 profiles
performed along the East Pacific Rise. It was found for the
first time between 12°N and 15°N [Charlou et al., 1988] on the MAR
and remained unexplained at that time. Similar CH4 profiles were
again found during the Ridelente cruise in 1988 between 15°N
and 23°N at many places (Figure 7), indicating that they appear to
be a common feature along the MAR.

Hydrothermal Activity in Other Areas Between 12° and 23°N

Twenty CTD stations (Figure 7) were carried out between
15°N and 23°N during the Ridelente cruise in 1988. RD-HY-04
on the eastern ridge axis/15°20'N FZ intersection shows a CH4
maximum anomaly (3.4 nmol/kg) in a 1-km-thick (2500-3500 m)
plume centered around 2900 m depth, 1 km above the seafloor.
Similar CH4 profiles were obtained on the western ridge
axis/15°20'N FZ intersection at stations RD-HY-05 (2.72 nmol/kg
at 3100 m), RD-HY-06 (3.70 nmol/kg at 3250 m), and RD-HY-
08 (2.50 nmol/kg at 3400 m). RD-HY-07 profile in the inner floor
shows a different CH4 signature with a regular linear increase
(0.44-1.34 nmol/kg) from 2000 m to the seafloor around 4000 m,
while RD-HY-09, located approximatively at the same latitude
but in the off-axis Royal Trough, is similar to a reference profile.
The stations RD-HY-10 and RD-HY-11 located in the axis at
16°37.42'N and 16°91.68'N, respectively, show CH4 profiles
with a first strong anomaly (1.83 nmol/kg) around 2500 m, a second
smaller anomaly (1.16 nmol/kg) around 3020 m, and a regular
increase down to the seafloor (1.12 nmol/kg at 4200 m). RD-HY-
12 and 13 profiles show a sharp jump in CH4 content from
background (0.44 nmol/kg) to 0.98 nmol/kg at around 2800 m
depth, which remains constant down to the seafloor at 3500 m.
RD-HY-14 is a reduced plume (maximum CH4 = 0.98 nmol/kg)
with characteristics similar to plumes observed at stations RD-
HY-04, 05, 06. Between 18°N and 20°N (RD-HY-16, 17, 18, 19,
20), CH4 anomalies are very small. However, a regular increase
in concentration is observed from 2000 m (0.44 nmol/kg) to the
bottom (0.89 nmol/kg). RD-HY-21 represents a CH4 profile near
background, even though a slight anomaly can be detected at
around 3000 m depth. Farther north, CH4 anomalies (0.89
nmol/kg) are again clearly defined on RD-HY-22 and 23 between
the

CH4 profiles

CH4 profiles

CH4 profiles
Fig. 5. Water column stations conducted on the east wall and axial dome close to the 15°20′N FZ/Ridge axis intersection during MAR/88 cruise (1988). The Sea Beam map was established during the Ridelente cruise (1988). The solid lines represent the CTD tracks and the open squares ate the upcasts at the end of tows. K01 (14°53.8′N-45°01.6′W) and K02 (14°55.0′N-44°59.0′W) are Klinkhammer’s lowerings during MAR/84 cruise [Klinkhammer et al., 1985]. HY-04 is a Ridelente station in this area. The dashed lines represent the 15°20′N FZ and the Ridge axis. A, B, C, D, are domes rising up to 1500 m above the inner floor of the valley. A and B are serpentininite structures.

2800 and 3000 m depth. RD-HY-15 and RD-HY-26, located at about 30 miles east of the ridge axis and in the Kane FZ respectively, show typical background CH₄ profiles. Except for these two profiles, all other profiles show significant but variable CH₄ anomalies along this MAR section. In addition, it can be observed that a CH₄ peak (0.89 nmol/kg) is also present between 2000 and 2500 m depth on the off-axis profiles RD-HY-01, 02, 03 carried out during a transit across the ridge axis. Significant CH₄ anomalies are present everywhere along the axis of this MAR section. They are observed in the 1-km-high layer above the seafloor and also at rift mountain levels (2000-2700 m), particularly between 16°N and 17°N where CH₄ degassing is intense (Figure 9).

These results are compared to CH₄ anomalies (up to 2 nmol/kg) previously found in the water column between 12° and 15°N [Charlou et al., 1988]. The large amplitude of the CH₄ anomaly at one station (HY-36), integrated over more than 1000 m, reflects a large CH₄ input and then extensive hydrothermal activity on the inner floor and the valley walls. The occurrence of a small CH₄ anomaly at about 2500 m at the three sites between 12°44′N and 14°05′N with the same amplitude over more than 2° in latitude was not explained [Charlou et al., 1988]. However, we think now that this 2500 m anomaly encountered at three stations between 12°N and 15°N, in all CTD tows conducted around the 15°05′N dome and confirmed on many other sites between 15° and 23°N along the MAR reflects an association between serpentinization and hydrothermal activity, with hydrothermal discharge on the top of the rift mountains (see discussion). This correlates well with the recovery of serpentinites in many dredges on the walls of the ridge at 14°43′N-45°00′W (2T-D-46 dredge, R/V Akademik Boris Petrov, 1985), at 15°36′N-46°35′W and 16°52′N-46°27′W, (RD-87-DR-08 and RD-87-DR-13 dredges, respectively, R/V Jean Charcot, 1988).

**DISCUSSION**

**CH₄ Plume Geometry on the MAR (Figure 8)**

CH₄ venting is clearly demonstrated near the seafloor along a 1200-km-long section of the Mid Atlantic Ridge. The two active areas known at the present time (TAG and MARK) generate typical CH₄ plumes rising up to 300 m above the seafloor in the rift valley. However, the various CH₄ profiles observed along the MAR (Figure 8) show the thickness of the hydrothermally affected seawater column is up to 1 km, approximatively 3 to 4 times thicker than on the EPR [Charlou et al., 1991a], Juan de Fuca Ridge [Baker et al., 1990], or the Lau Basin [Charlou et al., 1990b]. Differences in plume structure may be caused by differences in local current speed, entrainment rates, average vent orifice size, and vent fluid density [Turner and Campbell, 1987].
Fig. 6. Vertical profiles of CH₄ for stations in the 15°N area. The CH₄ profile (RD-HY-04) (open circles) obtained during the Rideleute cruise (1988) is superimposed on the CH₄ profile of cast 11 (solid circles) obtained during MAR/88 cruise to show the good concordance between the 1985 and 1988 profiles. CH₄ concentrations are elevated (up to 6.7 nmol/kg) in cast 15 conducted just above dome A (Figure 5). CH₄ plumes show maxima CH₄ anomalies at 3000 and 2500 m depth.

Fluid characteristics, residence time of elements, and combined effects of recent plumes mixed with old ones may produce different CH₄, He or Mn plumes [Charlou et al., 1991a]. Typical reference profiles found on the MAR and the EPR are presented respectively on Figures 8a and 8b. Figure 8c shows the CH₄ profile observed at HF-19 station (Hydrofast cruise) [Charlou et al., 1991a] near the 13°N hydrothermal site on the EPR. The CH₄ plume is 300 m high and anomalies reach 8 nmol/kg. A different large hydrothermal plume rising more than 800 m above the seafloor and extending several miles was identified by Horibe et al. [1986] along the axial region of the Mariana Trough (Figure 8d). The different shapes of the CH₄ plume observed along the MAR between 15° and 23°N are shown in Figures 8a and 8b. The vertical CH₄ distribution between 15°N and 23°N along the MAR is distinct in both structure and intensity from that found along the EPR, such as at 13°N (Figure 8c). EPR and MAR cross sections show that the EPR is characterized by a shallow (100-200 m) and narrow (200-500 m) axial graben on a topographic high while the MAR is characterized by a deep (1500-2500 m) and wide (10-20 km) axial valley. The composition, temperature, and thus the buoyancy of fluids from black smokers in both cases are similar [Donval et al., 1989; Edmond et al., 1990]. Because neutral buoyancy of the plume is achieved below the tops of the walls of the MAR rift valley [Trefry et al., 1985; Klinkhammer et al., 1986; Nelson et al., 1986].
The CH4 anomalies observed at different levels in a 1000-m layer above the seafloor of the MAR (Figures 8e, 8f, 8g, and 8h) indicate the presence of hydrothermal circulation in the inner floor (plumes clearly identified near the 15°20'N and Kane FZ), whereas those from the walls and/or at the top of the rift mountains (between 16° and 17°N) are located around 2400-2600 m depth (Figure 9). CH4 degassing is variable in intensity and correlated with the presence of ultrabasic rocks (Figure 11). It is lower on the tops of the walls than from the inner floor. The strength of CH4 degassing decreases progressively from the inner floor to the top of the rift mountains. In addition, no CH4 anomaly was observed within fracture zones.

Seawater-Basalt Interaction at TAG and MARK

On the slow spreading MAR, studies at TAG since 1972 and MARK since 1985 have established that a complete and active hydrothermal system is present at both sites, including black and white smokers similar in mineral composition to those observed on the EPR, with an intense but variable CH4 degassing. On the EPR, the fluids extract light volatile elements such as H2, He, and CH4 directly by leaching hot fresh basalt where these gases are present in great quantities. CO2 and H2S in the 350°C fluids are in the range of 5-10 mmol/kg, while CH4 and H2 have been measured up to 0.1 and 2 mmol/kg [Kim et al., 1988; Welhan and O'Nions, 1989, 1993]. Similar results were

Fig. 7 (continued).

Fig. 7. CH4 versus depth for stations sampled between 12° and 23°N during the Ridelente cruise (1988).

Fig. 7 (continued).
CHARLOU AND DONVAL: HYDROTHERMAL METHANE VENTING ON MID- ATLANTIC RIDGE

Fig. 8. CH4 plume geometry observed along the Mid-Atlantic Ridge. (a) Typical CH4 depth profile in the Atlantic Ocean without any detected anomaly. Station HY-14: 13°20.87'S-14°05.51'W; depth: 3570 m [after Charlou et al., 1987]. (b) CH4 depth profile at a control station in the Pacific Ocean [after Charlou et al., 1991a]. (c) Hydrothermal CH4 plume observed in the 300 m layer above the seafloor at 13°N on the East Pacific Rise [after Charlou et al., 1991b]; a biological peak is observed in the 500-700 m layer in this denitrification area (J.L. Charlou personal communication, 1990). (d) CH4 plume in the Mariana back arc spreading center [after Horibe et al., 1986]. (e) MAR CH4 anomalies observed in a 1-km-high layer above the seafloor (Ridelente cruise stations RD-HY-04, 05, 06, 08, 14, 22, 23, 24, 27, (this work). (f) Intense CH4 degassing on the top of rift mountains around 2500 m depth) and regular increase to the seafloor (station RD-HY-10 of the Ridelente cruise, (this work)). (g) Profile showing two clearly defined CH4 plumes (stations RD-HY-07, 11 of the Ridelente cruise, (this work)). (h) CH4 degassing from the walls of the ridge axis (stations RD-HY-12, 13, 16, 18, 19, and 20 of the Ridelente cruise).

al., 1989; Butterfield et al., 1990] (Table 3). Hydrothermal systems in sediment-hosted submarine rift systems are capable of generating and transporting major concentrations of volatile hydrocarbons. In Guaymas Basin, Gulf of California, the hydrothermal fluids percolate through the overlying sedimentary layer which is enriched in organic matter. The hydrothermal system converts immature organic matter in the overlying sedimentary cover to petroleum (methane to asphalt) [Simoneit et al., 1988]. In this case, CH4 has a clearly thermogenic origin as indicated by Ci/(C2-C5) concentration ratios (<500) and isotopic data [Welhan and Lupton, 1987]. Migration of the formed hydrocarbons occurs by dispersal in vent fluids and as a bulk phase in the sediments. The more soluble and volatile hydrocarbons are released into the seawater column by rapidly venting fluids and rise as large plumes [Welhan and Lupton, 1987].

At TAG and MARK sites, just as for EPR fluids, fluids circulate through young hot basaltic material without interaction with organic-rich sediment. The CH4/3He ratio of 2.6x10^6 found in Snakepit fluids [Jean-Baptiste et al., 1991] is similar to the CH4/3He ratio found in MAR basalt glasses (0.7x10^6) and in MAR volcanic "popping rocks" (2.1x10^6) [Welhan and Craig, 1983; Pineau et al., 1976], suggesting a nonbiogenic origin of CH4 in this area. The CH4 enrichment is not due to a thermocatalytic decomposition and oxidation of organic matter but seems to be produced probably by an outgassing of juvenile carbon as for helium, or via high temperature (>300-400°C) inorganic synthesis involving CO2 and H2.

TDM and CH4 in the Serpentinization Process: TDM/CH4 Covariation

Some discrepancies have been shown to exist between total dissolvable manganese (TDM) and CH4 in plumes, which can be explained by the characteristics of vent fluids, by their residence time in seawater, by different scavenging and oxidation kinetics, or by biological activity [Charlou et al., 1991a]. However, different TDM/CH4 ratios found for different vents or vent fields are explained by the large variations of solution properties or by seawater-rock chemical interactions which produce different hydrothermal solutions. The least squares correlations between TDM and CH4 concentrations and nephew's concentrations in plumes over TAG and the 15°05'N area are shown in Figure 10. In each case, TDM exhibits a linear relationship with CH4, but with quite different slopes corresponding to 3.60 mol/mol at TAG and 0.11 mol/mol, respectively, over the 15°05'N area. Accounting for data in hand so far, it must be noted that the range of TDM/CH4 is lower for TDM/CH4.
Fig. 9. Methane fields between 1600 m and the seafloor along the section 15°36’N / 23°N of the MAR. CH₄ plumes in the inner floor are clearly identified near the 15°20’N and Kane FZ. A CH₄ plume emitted at the top of rift mountains (2500 m) is defined around 16°30’N. Sample depths are indicated by dots (bottle data). The bathymetry of the ridge axis is schematic and very expanded.

| TABLE 3. CH₄ End-members in Hydrothermal Fluids Compared to CH₄ Content in MORB Glasses |
|---------------------------------|----------|---------------------------------|
| **Location**                    | CH₄ μmol/kg | **References**                   |
| Hydrothermal Fluids             |           |                                 |
| TAG (26°N) MAR                   | 144       | This work                       |
| Snakepit (23°N) MAR              | 62        | Jean-Baptiste et al. [1991]     |
| MARK Vent (23°N) MAR             | 45        | This work                       |
| 11°N EPR                        | 67 - 117  | Kim et al. [1984]               |
| 13°N EPR                        | 27 - 54   | Merlivat et al. [1987]          |
| 21°N EPR                        | 58 - 90   | Welhan and Craig [1983]         |
| Galapagos                       | 85 - 301  | Welhan and Lupton [1987]        |
| Guaymas Basin                   | 12150 - 16650 | Welhan and Craig [1983]         |
| southern, JDFR                  | 81 - 117  | Evans et al. [1988]             |
| Axial Seamount, JDFR            | 25        | Butterfield et al. [1990]       |
| Endeavour, JDFR                 | 504 - 1413 | Welhan et al. [1989]            |
| Lau Basin                       | 3.6 - 4.5 | Charlou et al. [1992c]          |
| MORB Glasses                    |           |                                 |
| MAR basalt glass                | 2.2 - 13.5 | Welhan and Craig [1983]         |
| EPR basalt Glass                | 0.6       | Welhan and Craig [1983]         |
| MAR popping rocks               | 12.6      | Welhan and Craig [1983]         |
Fig. 10. Evidence of different hydrothermal processes from TDM/CH₄ and Nephel/CH₄ ratios at TAG (26°N) and 15°N area [Charlou et al., 1991c; Rona et al., 1992]. Nephel measurements are from P. Appriou (University of Brest, France). These data were obtained during NOAA MAR/88 cruise (1988).

TDM/CH₄ CORRELATION

NEPHELOMETRY/CH₄ CORRELATION

than elsewhere. TDM anomalies have been reported [Klinkhammer et al., 1985] to be smaller along the MAR than those previously observed near venting areas on the EPR. Nevertheless, the range of CH₄ concentration on the MAR (this work) is similar to that encountered elsewhere. The significant difference in TDM/CH₄ ratio on the MAR is due to the wide range of TDM concentration [Klinkhammer et al., 1985, 1986; Jones et al., 1981; Jones and Murray, 1985; Boulegue and Hamelin, 1983; Bougault et al., 1990a,b, this issue; Charlou et al., 1991a,c]. The particularly low TDM/CH₄ ratio found in plumes over the 15°05'N area on the MAR is probably characteristic of the emitted fluids. This low ratio can be explained in terms of interaction between seawater and ultramafic rocks. In the 15°05'N area, intense CH₄ degassing and low TDM concentrations (Figure 10) are related to an axial dome (Figure 5) composed of serpentinized peridotites [Bougault et al., this issue]. A similar result was also obtained at 15°36'N in the inner floor of the MAR [Bougault et al., 1990a]. Serpentinized peridotites drilled during ODP leg 82 in the North Atlantic have been shown to be Mn-depleted (MnO = 0.08-0.12%) compared to MORB basalts (MnO = 0.16%) [Michael and Bonatti, 1985]. Similar results were observed recently during ODP leg 125 in the Mariana Forearc [Motti and Haggerty, 1989; Haggerty, 1991]. Drilling into the flank and the summit of a serpentinite seamount (Mn depleted; MnO = 0.06 to 0.10%) confirmed the presence of basic fluids (pH=12.5) enriched in CH₄ and light hydrocarbons. Seawater was identified as seeping through the serpentinite seamount at low temperature (13°C) with the formation of aragonite, calcite, and amorphous Mg-silicate. At TAG and MARK, as on the EPR, basalt-seawater interaction produces acid pH solutions with high TDM (up to 1 mmol/kg) and CH₄ (up to 144 μmol/kg) concentrations (Table 3). In the 15°N area, the interaction between seawater and ultramafic rocks may give basic pH solutions which are highly enriched in CH₄, and are associated with aragonite and carbonate deposits dredged from the western intersection (Ridelente cruise, 1988). The 1990 Akademik Boris Petrov cruise recovered massive aragonite-chrysotile hydrothermally cemented breccias and fragments of an apparent carbonate chimneys at the base of a steep scarp on the inside corner high at the eastern intersection (cruise report, 1990). The low TDM content in the 15°05'N plumes can be explained in terms of interaction of seawater with a Mn-depleted ultramafic material and/or Mn precipitation in the basement during the ascent of basic pH fluids in the hydrothermal/serpentinization process.

A direct mantle origin and a serpentinization origin can both be compatible to explain the high CH₄ concentration at 15°05'N and in other serpentinized areas along the MAR. The serpentinization process stipulates that water of crustal origin reacts with mafic-ultramafic rocks, and the low oxygen fugacity, resulting from hydration and oxidation reactions, leads to the stabilization of reduced gas species. Any carbon present during these reactions (i.e., intrinsic carbon in the rocks or dissolved carbon in solution) is thus converted to CH₄. The ultramafic rock-seawater interaction as observed on the axial serpentinite dome (15°05'N) generates solutions with a high CH₄ content, probably associated with H₂ and CO₂ gases. Therefore, if the major element chemistry of the peridotite is generally not significantly modified by serpentinization at temperatures below 500°C, serpentinization in CO₂-rich fluids at 300°C, 500 bars results in the generation of H₂ and in partial conversion of CO₂ to hydrocarbons [Janecky and Seyfried, 1986; Abrajano et al., 1988; Szatmari, 1989]. In addition, H₂ can be generated by a reaction at a high temperature between water and silica radicals, by reduction of water by hot (>800°C) ferrous rocks [Apps, 1985] and by outgassing from Earth's mantle rocks under stress. Volume expansion resulting from serpentinization of ultramafic rocks also may promote development of fracture systems that could further enhance water-rock reaction. Significant quantities of H₂, formed by the reduction of H₂O during serpentinization, have been observed on the surface in peridotites of the Oman ophiolites [Neal and Stanger, 1983], in the subsurface over the U.S. mid-continent gravity anomaly [Coveney et al., 1987], and in experiments [Janecky and Seyfried, 1986]. The occurrence of free H₂ as shown on the MAR supports the hypothesis that this fluid is produced in situ at TAG.
hydrocarbon generation by hydrogenation. The reduction of CO₂ through the Fischer-Tropsch synthesis produces CH₄ and unsaturated hydrocarbons. In conclusion, conditions under which CH₄ can be produced occur where there are adequate supplies of carbon and a suitable reductant (such as H₂, Fe⁺² or Fe°). These reduced gas occurrences are closely associated with mafic-ultramafic rocks. The presence of H₂-CH₄ gas seeps in serpentinized mafic-ultramafic rocks suggests a possible correlation between reduced gas formation and serpentinization. Magnetite, serpentine, brucite, and H₂ gas are produced during serpentinization of olivine [Abrajano et al., 1988]. Mantle carbon in mafic-ultramafic rocks can take the form of solid phases (graphite) or fluid species (e.g., CO₂, CO, CH₄) trapped as fluid inclusions. The graphite crystals recovered in the vicinity of hydrothermal vents at 13°N on the EPR were formed during serpentinization by reaction of CO and/or CO₂ [Jedwab and Boulegue, 1984], and graphite was also identified in partly serpentinized Zambales ultramafic rocks [Abrajano et al., 1988].

Hydrothermal Activity, Serpentinization, Mantle Degassing Between 12° and 26°N on the MAR

CH₄ profiles between 12° and 26°N show that hydrothermal activity is present everywhere along this section of the MAR, is variable in intensity and not randomly distributed, and is at a maximum near the fracture zones (Kane FZ, eastern and western 15°N FZ/ridge axis intersections), where the permeability favors downwelling of seawater and serpentinization of ultramafic rocks (Figure 9). At 15°05’N, the CH₄ maximum due to hydrothermal activity is correlated with the occurrence of serpentinized ultramafic rocks on structures located within the axial domain of the rift valley (Figure 11). This observation suggests that seawater and fluids reach the crust/mantle interface. Ultramafic rocks are serpentinized and reach the surface. The density of this layer is lowered by hydration, and serpentinized ultrabasics bodies are uplifted as diapirs (clearly mapped at 15°05’N) controlled by the tectonic structure [Bougault et al., 1990a,b, this issue]. These diapirs form dome-shaped features in the rift valley and adjacent fracture zone. CH₄ anomalies observed in surrounding plumes show that hydrothermal discharges appear to be preferentially distributed around and on the seafloor domes. The upwelling hydrothermal circulation follows crust-penetrating faults that may have controlled the diapirc ascent of the serpentinites and that continue degassing magma and/or mantle [Rona et al., 1987]. The solution properties may have evolved either by cooling and metal depletion of high-temperature end-member solutions that reacted with deep ultramafic rocks or by shallow low-temperature reaction of seawater with serpentinized ultramafic and mafic rocks. A spectrum of hydrothermal solution properties exists, controlled by the reaction of convectively circulating seawater with different portions of the oceanic lithosphere related to

![Fig. 11. CH₄ variation between 14°N and 23°N along the MAR. The schematic ridge axis (after H.D. Needham, unpublished data, 1987) is represented on the left side. Solid triangles and open circles show respectively basalts and ultramafic rocks collected in dredges conducted in the CTD/cast areas. Solid circles represent maximum CH₄ concentration measured on each profile in two seawater layers: CH₄ maxima in the (2700-m bottom) layer (lower peak) in the middle, and CH₄ maxima in the (2400-2700 m layer (upper peak) on the right side of the figure. CH₄ background is 0.36 nmol/kg in Atlantic deep waters.](image-url)
different tectonic settings along the Mid Atlantic Ridge [Rona et al., 1992].

**SUMMARY AND CONCLUSIONS**

In spite of its nonconservative property, CH₄ is a good tracer of hydrothermal activity along mid-oceanic ridges. CH₄ plumes obtained every 20-40 km between 12° and 26°N on the MAR show a variability in shape and intensity. The morphology of the ridge axis has a strong influence on the geometry of the observed CH₄ plumes. These CH₄ plumes have maxima above the two vent fields (TAG and MARK) known at the present time. The shape of CH₄ profiles clearly shows the water depth of sources, with CH₄ degassing in the inner floor near the bottom, on the rift axis walls and on the top of the rift mountains.

In addition, the qualitative relationships between CH₄ and other chemical tracers (i.e., TDM/CH₄) contribute to determination of the distribution, type, and chemical composition of vents along a spreading ridge segment and may provide information on the subseaflow processes involved in mantle structure and mechanisms which form the ridges. CH₄ and TDM data obtained along the MAR show that different TDM/CH₄ ratios are found on the MAR (i.e., TAG and 15°05'N area). These different ratios obtained between two nonconservative tracers provide a useful framework for identifying and differentiating subseaflow processes along mid-oceanic ridges. The high TDM/CH₄ ratio found above TAG and MARK areas is indicative of basalt-seawater interaction, while at 15°05'N the low TDM/CH₄ ratio provides evidence of fluid circulation in ultramafic rocks.

CH₄ profiles between 12° and 26°N show that hydrothermal activity is present everywhere along this section of the MAR, is variable in intensity, not randomly distributed, and is maximum near the fractures zones. Enhanced permeability at the intersections of the rift valley with the fracture zones favors downwelling of seawater and serpentization of lower crustal and upper mantle ultramafic rocks. CH₄ investigations reveal and confirm the association between hydrothermal activity, serpentization, diapirism and mantie degassing along the Mid-Atlantic Ridge.

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