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Methane anomalies over TAG hydrothermal field on Mid Atlantic Ridge

by J. L. Charlou,[1] P. Rona[2] and H. Bougault[1]

ABSTRACT

Black smoker type hydrothermal venting was discovered in July 1985 at the TAG hydrothermal field in the rift valley of the Mid Atlantic Ridge near 26N. We present here, the first methane profiles in the seawater column over this black smoker along with methane profiles away from the black smokers for comparison. The CH_4 plume, spreading over 400 m above the seafloor, shows a maximum concentration of 105 nl/l at 3450 m (238 m above the bottom), correlated with a positive temperature anomaly (0.02°C). CH_4 concentrations up to 2422 nl/l, correlated with a huge positive increase of *in situ* temperature (0.349°C), have been measured in samples taken 5 m above the sea floor, showing an important CH_4 input in this slow spreading site which is similar to inputs from fast spreading sites like the East Pacific Rise.

1. Introduction

Injection of hydrothermal fluids to the ocean occurs in the axial zone of ocean ridges by discharge from vents. Hydrothermal solutions have been studied in samples recovered by submersible in black smokers at several sites on the East Pacific Rise (Edmond *et al.,* 1982; Michard *et al.,* 1984). Although these samples were more or less mixed with sea water, it has been demonstrated that the end-member fluids are highly enriched in the gases helium, methane and hydrogen (Welhan and Craig, 1979, 1983) and in dissolved iron and manganese. Methane in hydrothermal solutions is generally believed to result from degassing of the mantle or from abiogenic water-rock-interaction (Welhan and Craig, 1983), as well as from biogenic production by bacteria (Lilley *et al.,* 1983) and thermocatalysis of organic matter in sediments (Welhan and Lupton, 1987). Extrapolated end-member fluids have CH_4 concentrations ranging from 3.4 $\mu M/l$ at the Galapagos spreading center (Lilley *et al.,* 1979) to 80 $\mu M/l$ at the 11N and 13N EPR hydrothermal vent fields (Welhan *et al.,* 1984). (1μM CH_4 = $2.24 \cdot 10^{-2}$ ml/l CH_4 STP.)

Because of huge enrichment factors and in spite of dilution of hydrothermal solutions by sea water, hydrothermal activity produces some concentration anomalies

in the deep ocean waters. As for helium and manganese, excess methane in the seawater column persists for a sufficiently long time to use these anomalies to detect active hydrothermal areas. Emission from the world oceanic ridge system, estimated by extrapolation from the East Pacific Rise data (Welhan and Craig, 1979, 1983), amounts to $1.6 \cdot 10^8$ m^3 of CH$_4$ a year. The mean concentration of deep ocean methane is only about $3 \cdot 10^{-6}$ ml kg^{-1} in deep Pacific waters and $6 \cdot 10^{-6}$ ml kg^{-1} in deep Atlantic waters (Lamontagne *et al.*, 1973). Consequently, the calculated average global injection rate of CH$_4$ into the oceans indicates a residence time of the order of 30 years, implying that consumption of CH$_4$ in the water column must be rapid.

Over the East Pacific Rise (fast spreading) the existence of submarine hydrothermal convection systems has been confirmed by the discovery of hydrothermal plumes over the Galapagos spreading center (Weiss, 1977), 13N (Boulegue *et al.*, 1980), 21N (Lupton *et al.*, 1980), 15S (Lupton and Craig, 1981), Juan de Fuca Ridge (Normark *et al.*, 1982; Baker *et al.*, 1985) and Guaymas Basin (Londsdale *et al.*, 1980). Evidence for the existence of hydrothermal plumes at these sites has been obtained by physical measurements of water temperature anomalies, level of suspended particulate matter detected with nephelometry, and by analysis of geochemical tracers in the seawater column. Helium, manganese and, more recently, methane have helped to find and characterize the injections of mantle volatiles over these active hydrothermal zones.

Recently reported hydrothermal activity for slow spreading oceanic ridges in the North Atlantic Ocean, western Indian Ocean and northern Pacific Ocean (Gorda Ridge) suggests that hydrothermal venting may exist along all such slow spreading ridges. Previous evidence for hydrothermal activity at the Mid Atlantic Ridge from 10N to 26N was substantial. It was well documented by manganese concentrations in ocean water (Klinkhammer *et al.*, 1985a), temperature anomalies (Lowell and Rona, 1976), manganese deposits (Scott *et al.*, 1974), heat flow anomalies in the sediment column, photographic evidence, dredged rocks and enriched metalliferous sediments (Cronan *et al.*, 1979), ^{3}He/^{4}He ratios in the water column (Jenkins *et al.*, 1972, 1980), photographs of vent organisms (Rona *et al.*, 1984; Kong *et al.*, 1985) and more recently from CH$_4$ anomalies in sea water between 12 and 15N (Charlou *et al.*, 1986).

The first black smoker-type hydrothermal venting at the TAG hydrothermal field in the rift valley of the Mid Atlantic Ridge near 26N was discovered in July 1985 (Rona, 1985; Rona *et al.*, 1986). Shipboard measurements of elevated concentrations of dissolved manganese (Klinkhammer *et al.*, 1985b) and of light scattering by suspended particulate matter in the water column (Nelsen *et al.*, 1985; Trefry *et al.*, 1986) indicated ongoing hydrothermal activity. A systematic survey with a deep-towed instrumented sled located the black smokers by measuring near-bottom water temperature anomalies and recording seafloor images (Rona, 1985; Rona *et al.*, 1986). We present here the first methane profile in the seawater column over the black smokers at the TAG Hydrothermal Field, along with methane profiles away from the black
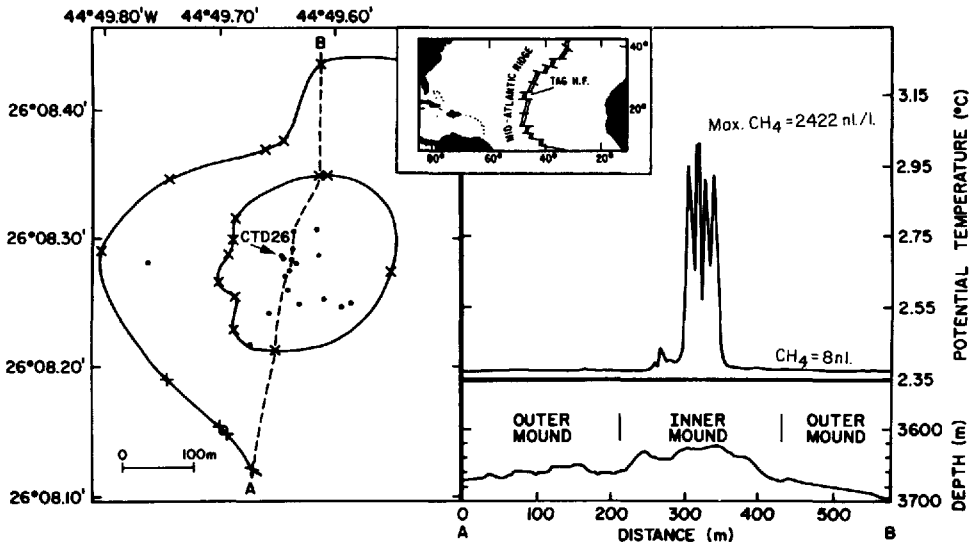
Figure 1. Illustrations showing location and characteristics of site of black smokers where water samples were recovered with CTD 26 at the TAG Hydrothermal Field in the rift valley of the Mid Atlantic Ridge (modified from Rona *et al.*, 1986). Index map (top center) shows the location of the TAG Hydrothermal Field at the Mid Atlantic Ridge crest at latitude 26N. Illustration at left is map showing outer and inner boundaries of a mound delineated by multiple crossings (x) with near-bottom camera-temperature-tows, the distribution of black smoker-type hydrothermal vents (dots), the location of CTD 26, and the trackline of the towed instrument transect (A–B). Illustration at lower right is a bathymetric profile across the mound along the transect (A–B). Illustration at upper right is a potential temperature profile in the water column within 10 m of the sea floor along the transect (A–B); the four central spikes correspond to crossings of black smokers.

smokers for comparison. The profile was made over one of a cluster of at least eleven black smokers that discharge from fractures in the central portion of a mound about 250 m in diameter and 50 m high composed primarily of hydrothermal precipitates including massive sulfides (Fig. 1) (Rona *et al.*, 1986). The mound lies along faults at the juncture between the base of the east wall and the floor of the rift valley at water depths between 3620 and 3700 m. The black smoker site is contiguous with a previously known zone of lower temperature hydrothermal discharge associated with iron- and manganese-rich, hydrothermal precipitates higher on the east wall of the rift valley between water depths of 2500 and 3100 m (Rona *et al.*, 1984).

2. On-board sampling and storage of samples

During NOAA Vents Program cruise, seawater samples were collected at three stations, ST2-CTD2, ST6-CTD9, and ST6-CTD26 near 26° on MAR (see locations on Fig. 3, 4) for CH_4 analysis on shore. The seawater samples, obtained by using Niskin

301 bottles mounted on a CTD/Rosette, were transferred by gravity flow into 250 ml gas analysis bottles with teflon stopcocks. The bottles were filled from below and allowed to overflow vertically about one third of their volume in order to avoid trapping air bubbles. For long storage of the samples, it is necessary to inhibit microbial activity, by poisoning. All samples were poisoned with sodium azide when collected and shipped by air to IFREMER laboratory (Brest-France) at the end of the cruise.

Methane analyses were performed immediately after receipt in the laboratory by the modified method of Swinnerton *et al.* (1962), as described by Scranton and Brewer (1977). Some contamination by air may have occurred during storage. The effect of storage for periods of a few weeks to several months before analysis has been studied for Caribbean Sea and Gulf of Maine poisoned samples (Scranton and Brewer, 1977) and on poisoned Pacific water samples (Charlou, 1986b). The comparison of results obtained at sea with those obtained later in the laboratory shows small variations. All samples with high methane concentrations (2 to 8 μM/kg) lost methane (up to 15%). The deep samples with low methane concentrations (0.2 to 1 nM/kg) gained methane (2 to 5%). Samples which were nearly at equilibrium with the atmosphere (3.4–3.7 nM/kg) seemed to store well. However, it is clear that inaccuracies of this magnitude will not change the arguments to be made.

3. CH$_4$ extraction and chromatographic analysis

Methane extraction was carried out using a modification of the technique described by Swinnerton *et al.* (1962). The seawater samples were transferred under methane-free helium from the 250 ml glass bulb to a gas stripping system. The helium carrier gas was purified by passage through a molecular sieve-activated charcoal trap placed in liquid nitrogen. Dissolved gases were stripped from the sea water by purging with purified helium for ten minutes at a flow of 120 ml/minute and were concentrated on two $\frac{3}{16}$" o.d. stainless steel traps.containing respectively activated alumina for trapping higher than CH$_4$ hydrocarbons and activated charcoal for trapping CH$_4$ and CO. For this work, only CH$_4$ was analyzed. Because of the low concentrations of C$_2$ and C$_3$ hydrocarbons in sea water, a volume of 1 liter is necessary to analyze these compounds. When stripping was completed, a six way gas valve was turned to place the activated charcoal trap in line with a 4 ft $\frac{1}{8}$" o.d. stainless steel column packed with a 60–80 mesh porapak Q. The trap was placed in a hot bath at 100°C. By raising the trap temperature, the CH$_4$ was desorbed from activated charcoal and injected into a chromatographic column placed in the oven of an Intersmat Instrument chromatograph equipped with a flame ionization detector. Peaks were recorded and integrated on a ICR1B Shimadzu integrator. System calibrations were made by injecting known values of two calibration standard gases (L'Air liquide standard 2.1 ppm ±2% and 10 ppm ±2% in helium). The limit of detection of the method is 0.5 nl CH$_4$ (STP) per liter of seawater (1 nM = $2.24 \cdot 10^{-5}$ ml STP CH$_4$).
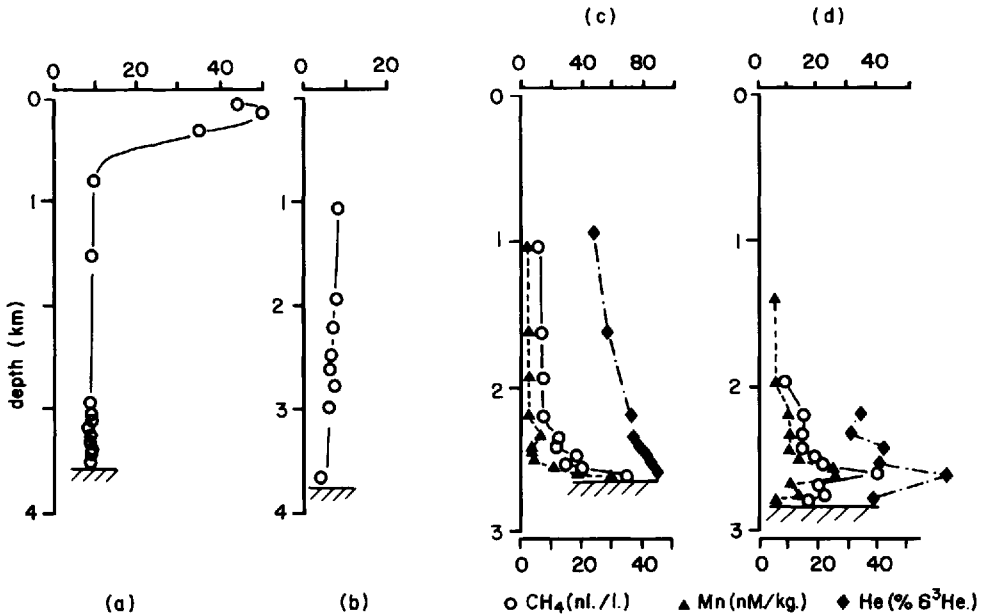
Figure 2. (a) Typical methane depth profile in Atlantic ocean without anomaly. Reference station Hy-14: 13°20'87 S – 14°5'51 W (Charlou *et al.*, 1986a). (b) CH$_4$ depth profile at a control station in Pacific Ocean. Station Hy-Cy-08 (Cyatherm cruise): 15°32'04 N–101°33'72 W (Charlou *et al.*, 1986a). (c) CH$_4$, He, Mn profiles over hot springs on the EPR at 12°50 N above the "Chain site"—Cyatherm cruise. Station Hy-Cy-01: 12°48'49N–103°56'39 W. (d) CH$_4$, He, Mn profiles on the EPR at 12°50 N site. This station Hy-Cy-05 was located 4 km west of the axis at 12°46'41 N–103°55'44 W. The hatched lines on Figure 2 a, b, c, d, indicate the bottom depth. Helium profiles are by Merlivat (CEA/Saclay–France).

4. Results

a. Methane profiles in the open ocean

Enrichment of CH$_4$ in surface waters is a common feature. Concentrations of CH$_4$ measured in samples from the mixed layer are commonly higher than concentrations predicted from the solubility of CH$_4$ in sea water and known atmospheric concentrations (Lamontagne *et al.*, 1973; Brooks *et al.*, 1973). The methane maxima in the upper seawater column indicates the existence of biological methane production at rates much faster than physical removal (i.e. diffusion to the atmosphere) and chemical or biological consumption. Typical profiles of methane versus depth in the open ocean are presented in Figures 2a, b for Atlantic Hy-14 and Pacific Hy-Cy-08 reference stations.

From 50% supersaturated concentrations in surface layers, CH$_4$ contents decrease regularly with depth to 8–10 nl/l at 1000 m. Deep North Atlantic waters have only

30% of their atmospheric equilibrium values of CH_4 (10 nl/l) and deep North Pacific waters have only 10% (4 nl/l) (Scranton and Brewer, 1978). Generally, in deep waters, typical concentrations are about 4 nl/l in the Pacific and 6–8 nl/l in the Atlantic (Lamontagne *et al.*, 1973). The value of 8 nl/l found at 2500 m at the three stations ST2-CTD2, ST6-CTD9, ST6-CTD26, near 26N on MAR is consistent with results of other authors.

b. CH_4 anomalies at fast spreading ridges: EPR

Large levels of CH_4 are found in anoxic basins (Lamontagne *et al.*, 1973; Atkinson and Richards, 1967) and at hydrothermal sites (Kim, 1983). In the Red Sea, CH_4 concentrations vary from 50 nl/l in the water column to 150 μl/l in brines (Burke *et al.*, 1981). CH_4 concentrations in hydrothermal end members at 10°50′N on the East Pacific Rise (EPR) (Welhan *et al.*, 1984) are from 10^5 to 10^6 times greater than normal deep ocean waters. This contrast is so great that CH_4 discharges on the sea floor create CH_4 anomalies in deep waters.

Figure 2c presents a profile at 12°50′N on the EPR above the "Chain site"; CH_4 enrichment up to 70 nl/l are observed close to the sea floor. The CH_4 anomaly is still clearly detectable 4 km west (Fig. 2d) of the site at about the same depth. A good correlation exists between helium, manganese and methane anomalies. Helium-3, a primordial isotope of helium, has proved to be a most sensitive tracer for the hydrothermal activities. The enrichment of the isotopic ratio provides a characteristic signature for mantle volatiles (Craig and Lupton, 1981). Manganese has also been used for tracing hydrothermal plumes. Manganese shows a linear relationship with helium-3 in the water column over the 21N hydrothermal system (Lupton *et al.*, 1980).

The amplitudes of CH_4 anomalies found to date vary between the different studied sites: 105 nl/l at Vulcan station 3 and 250 nl/l at Vulcan station 6 at 20S EPR zone; 60 nl/l on the 21N EPR zone at Pluto station 13, above the vent field, 74 nl/l in Marianna trough Cepheus 82 station 20 (Kim, 1983). During the Cyatherm cruise in 1982, we measured 70 nl/l above a vent field located at 12°50′N on the EPR axis (Fig. 2d) and up to 40 nl/l between 12 and 15N on the MAR (Charlou *et al.*, 1986a).

c. CH_4 anomalies at 26N, MAR

Cast station ST6-CTD9 (Fig. 3). Higher than normal temperatures were detected in the bottom waters. The anomaly of temperature (about 0.05°C) is very clear between 3250 m and 3561 m. In the last 300 m above the sea floor, the variability of temperature recording increased significantly. No such anomalies were observed at site CTD2 (abyssal plain).

Between water depth of 2500 m (CH_4 = 8 nl/l) and 3578 m, CH_4 concentration increases progressively from 25 nl/l at 3000 m, to 57 nl/l at 3165 m and 78 nl/l at 3417 m. A CH_4 plume has risen 400 m above the sea floor. The observed anomalies are
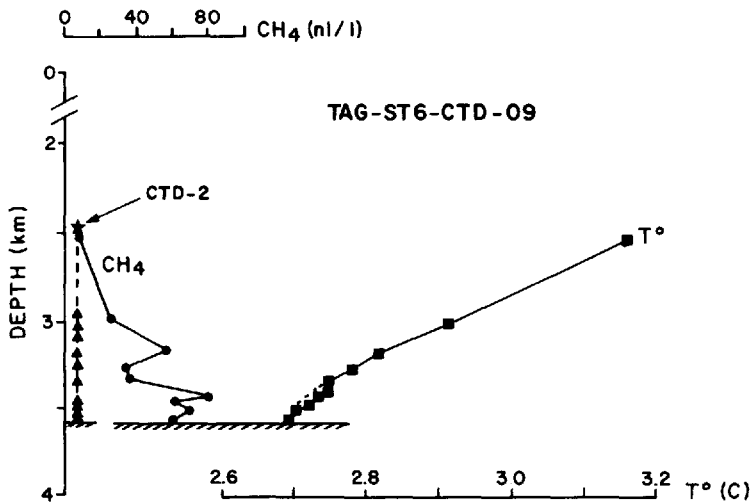
Figure 3. Cast station ST6-CTD9: Lat: 25°50.60′N–Long: 42°33.60′W. *In situ* temperature (°C) and methane concentration (nl/l) are represented versus depth (km). The hatched lines indicate the bottom depth (3578 m). Note the good correlation of CH_4 and temperature anomalies. The vertical dotted line (triangles) represents the typical background of CH_4 profile in deep Atlantic waters (6–8 nl) (see Hy14 station on Fig. 2). The star (*) represents a sample taken at 2500 m depth at station TAG-ST2-CTD2 (LAT: 26°09.50′; LONG: 44°48.40W).

10 times greater than normal CH_4 concentrations in deep waters and similar to EPR CH_4 anomalies.

Cast station ST6-CTD26 (Fig. 4). CH_4 concentration increases from 8 nl/l at 2500 m to 52 nl/l at 3578 m and 105 nl/l at 3450 m. After this maximum located at 238 m above the bottom, the CH_4 concentration decreases to around 58 nl/l at 3641 m (47 m above the bottom). Like in CTD-9, the CH_4 plume is spreading over 400 m above the sea floor. The CH_4 anomaly at 3450 m correlates with positive temperature anomaly (about 0.05°C). Very high CH_4 concentrations have been analyzed on two samples taken at 3672 m and 3676 m (12 m and 16 m above the sea floor). On the chromatographic recording, these CH_4 peaks show similar integrated areas corresponding to respective concentrations of 2402 and 2422 nl/l. These two very high CH_4 values correlate with an increase of *in situ* temperature from 2.680°C to 3.029°C (Δt = 0.349°C) at 5 m above the sea floor.

The CH_4 concentrations at ST6-CTD26 are about 400 times greater than typical CH_4 concentrations of deep Atlantic waters. These samples were collected with the CTD/Rosette system within tens of meters of a black smoker: despite this high CH_4 concentration compared to sea water, this result shows how rapid is the dilution of hydrothermal fluids with sea water, since CH_4 concentrations in the hydrothermal
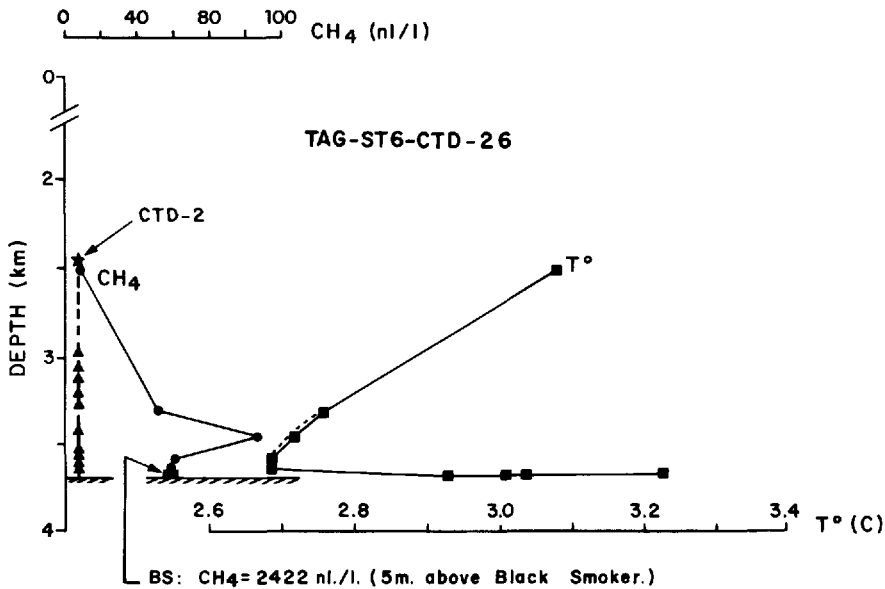
Figure 4. Cast station—ST6-CTD26: Lat: 26°08.28′N; Long: 44°49.65′W. *In situ* temperature (°C) and methane concentration (nl/l) are represented versus depth (km). The hatched lines indicate the bottom depth (3688 m). Note the good correlation of a CH_4 anomaly (105 nl/l) with a water temperature anomaly (about 0.02°C) at 3450 m depth. At 3676 m (12 m above the sea floor) the large temperature anomaly ($\Delta t = +0.55$°C; highest measured temperature was 3.37°C) corresponds to large concentration of CH_4 (up to 2422 nl/l) in two seawater samples taken just over the black smokers (BS). The sample taken at 3298 db depth is located at 150 m from vent. The vertical dotted line (triangles) represents the typical background CH_4 profile in deep Atlantic waters (6–8 nl/l) (see Hy14 station on Fig. 2). The star (*) represents a sample taken at 2500 m depth at station TAG-ST2-CTD2 (Lat:26°09.50′N; LONG: 44°48.40′W).

fluids are presently about 1–2 ml/l. It also demonstrates that a very large contrast between hydrothermal fluids and sea water is required before an element or compound can be used to identify plumes.

5. Conclusions

Methane measurements made on water samples collected near black smokers at the junction of the base of the east wall and the floor of the rift valley, near 26°08′N, 44°49′W, contiguous with a previously known zone of low temperature hydrothermal activity higher on the east wall, confirm the presence of a significant excess of CH_4 which is correlated with temperature anomalies (Rona, 1985) and excess of dissolved manganese (Klinkhammer *et al.,* 1985b), particulate iron, and total suspended matter (Trefry and Trocine, 1985).

The magnitude of these CH$_4$ excesses (up to 105 nl/l) in the seawater column, 200 to 400 m above the sea floor and especially the high CH$_4$ concentrations (around 2400 nl/l) found in two samples collected 10–15 m near the bottom (CTD26), are consistent with the presence of ongoing and well developed hydrothermal activity at this site, on the Mid Atlantic Ridge, similar to sites on the East Pacific Rise. These CH$_4$ concentrations are the largest CH$_4$ anomalies measured on samples collected by a surface ship with CTD/Rosette in the seawater column near the sea floor.

The largest CH$_4$ excesses, extending from 200 to 400 m above the bottom, show a significant vertical CH$_4$ gradient at the site studied. CH$_4$ concentrations up to 60 nl/l and elevated values of manganese (Klinkhammer *et al.,* 1985) measured 400 m above the sea floor in the two profiles indicate that these MAR vents generate buoyant plumes similar to those observed over the EPR. Horizontal mixing and advection also occur.

The large vertical extent of the CH$_4$ anomaly suggests continuous long term injection of fluids, involving an enrichment of sediment with pure hydrothermal metalliferous precipitates (Cu, Fe, Mn, Zn) within 2 km of the vent field (Trefry *et al.,* 1986). The CH$_4$ results obtained on seawater samples from the MAR between 12 and 15N (Charlou *et al.,* 1986a) and the samples studied here, show that active vents are present on slow spreading ridges that are similar to those on fast spreading ridges. On the EPR, the most recent volcanic activity primarily occurs in a faulted axial valley associated with metalliferous sulfide deposits. Hydrothermal edifices constructed of hydrothermal precipitates are present at a water depth of about 2600 m. On MAR, up to now, fluid emission has been found rising on the walls of the rift from a depth of about 3600 m (Charlou *et al.,* 1986a; this work); subsequent to this discovery at the TAG site, black smokers were found 310 km to the south at 3600 m at the axis of the rift valley of the Mid Atlantic Ridge (Leg 106 Scientific Drilling Party, 1986), indicating the high temperature hydrothermal venting may be a general feature of slow, as well as fast spreading oceanic ridges. Looking at the similarities of CH$_4$ profiles in the seawater column above active vents at sites on the two different types of ridges, we conclude that hydrothermal fluids of the MAR seem to be as enriched in CH$_4$ as hydrothermal fluids of the EPR. In order to compare the total CH$_4$ input along slow and fast spreading systems, it will be necessary to know the frequency of active vents along the ridge and the nature of emanating fluids. Therefore, collection of fluids by submersible is needed to advance knowledge of the hydrothermal exchange processes on slow spreading oceanic ridges. The high CH$_4$ concentrations found over the vents of 26N (TAG) indicate high temperature fluid injection comparable to high fluid injection of EPR. Analysis of the first hydrothermal fluid samples obtained in May/June of 1986 from two active vent sites at 26N(TAG) and 23N(MARK) on MAR confirm these observations. Despite the greater depth of these vents (3700 m) relative to those at 21N or 13N on EPR (2600 m), they display similar high temperature (300–350°C) and similar fluid composition (Edmond *et al.,* 1986). So,

high temperature venting on slow spreading ridges appears to be common. These first methane data in the seawater column associated to chemical data of hydrothermal fluids, contribute to our understanding of the role of pressure on the behavior of the fluids during seawater-rock interaction on fast and slow ridges.

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