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

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Hydrographic surveys along the Mid-Atlantic Ridge (MAR) between 12°N and 26°N, carried out from 1984 to 1990, show a variable pattern of CH4-rich water column plumes. The vertical distribution of CH4 at stations located every 20-40 km is presented along this 1200-km-long section of the MAR. CH4 venting is clearly demonstrated. CH4-enriched fluids rise from vents as plumes; spreading is confined to the axial valley due to the topography of the MAR. CH4 contents from 45 nmol to 675 nmol/kg are measured in the buoyant plumes above the two active hydrothermal sites (MARK 23°N; TAG 26°N) known at present, whereas CH4 anomalies up to 3.6 nmol/kg are typically observed in plumes emitted either on the inner floor, on the walls, and/or at the top of the rift mountains along the studied ridge section. CH4 concentrations (45 μmol to 144 μmol/kg) in MARK and TAG vent fluids are of the same order of magnitude as those found in the East Pacific Rise fluids. Even though CH4 is known to be unstable with respect to oxidation by dissolved oxygen, and in spite of its microbial oxidation in plumes, these results confirm CH4 to be a good indicator to track hydrothermal plumes and to map the variation of hydrothermal activity along mid oceanic ridges. Moreover, between 12° and 26°N along the MAR, CH4 results show that while hydrothermal activity is present everywhere along the ridge, it is predominant near fracture zones (FZ) (Kane FZ, 15°20'N FZ). Comparison of CH4 tracer with total dissolvable manganese (TDM) tracer in plumes allows us to differentiate subseafloor hydrothermal processes. The high TDM/CH4 found above TAG and MARK areas is indicative of basalt-seawater interaction, while at 15°N the low TDM/CH4 provides evidence of fluid circulation in ultrabasic rocks. CH4 data confirm the association between mantle degassing, hydrothermal activity, and serpentinization along this 12°-26°N section of the Mid-Atlantic Ridge.

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.*, 1985*a,b*; *Von Damm and Bischoff*, 1987; *Michard et al.*, 1984; *Campbell et al.*, 1988*a*], slow spreading ridges such as the Mid-Atlantic Ridge [*Rona et al.*, 1986; *Campbell et al.*, 1988*b*; *Jean-Baptiste et al.*, 1991], or back arc environments such as the North Fiji [Grimaud et al., 1991] and Lau [*Fouquet et al.*, 1990, 1991*a,b*; *Charlou et al.*, 1991*b*] 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.*, 1987*a,b*; *Fouquet et al.*, 1991*a,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.*, 1987*a*]. 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.*, 1985*a,b*; *Von Damm and Bischoff*, 1987], and in the gases helium, methane, and hydrogen [*Welhan and Craig*, 1979, 1983; *Lilley et al.*, 1982*a*; *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 [*Charlou et al.*, 1991*a*] or on the Juan de Fuca Ridge [*Baker and Massoth*, 1987; *Baker et al.*, 1987*a,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 [*Charlou et al.*, 1991*a*]. Particularly, the

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residence time of tracers in seawater can range from infinite (helium) to relatively short (Mn [*Emerson et al.*, 1982, *Cowen et al.*, 1986] and CH_4 [*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 ^3He 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 CH_4, H_2, Mn, and particles [*Kadko et al.*, 1990]. Microbial CH_4 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 CH_4 not to be a conservative tracer. Although CH_4 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 CH_4 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, 1991*a,b*; *Nojiri et al.*,1989; *Pluger et al.*, 1990].

In the Atlantic Ocean, CH_4 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 CH_4 in the seawater column along the Mid-Atlantic Ridge axis. Evidence of CH_4 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, 1991*c*], and at MARK site (23°N) during Hydrosnake cruise on the R/V *Nadir* with the submarine *Nautile* in 1989 [*Jean-Baptiste et al.*, 1991]. New findings obtained during the Ridelente cruise (1988), on the R/V *Jean Charcot*, Mid-Atlantic Ridge (MAR)/88 cruise (1988) on the NOAA ship *Oceanographer* and MAR/90 cruise (1990), and on the R/V *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 CH_4 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, CH_4 equipment was set up in a portable clean air-conditioned van, permitting CH_4 analysis every 15 min, 24 hours a day. The trapping method [*Swinnerton and Linnenbom*, 1967; *Scranton 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 C_2-C_4 hydrocarbons and activated charcoal for trapping CH_4 and CO, respectively. For this study, only CH_4 was analyzed. By raising the trap temperature, the CH_4 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 Liquide/Alfagaz CH_4 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 CH_4 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 CH_4 per kilogram of seawater. Taking into account the precision of the calibration, blanks correction, and reproducibility, the precision was +/-3% within a CH_4 concentration range of 0.22-18 nmol/kg.

CH_4 ANOMALIES IN DEEP WATER AT SPREADING AXES

In oceanic regions unaffected by hydrothermal inputs, deep waters are CH_4 undersaturated due to in situ consumption [*Scranton and Brewer*, 1978], and CH_4 concentrations decrease with depth to respectives backgrounds of about 0.18 nmol/kg in the Pacific and 0.36 nmol/kg in the Atlantic [*Lamontagne et al.*, 1973, 1974; *Swinnerton and Lamontagne*, 1974; *Kim*, 1983; *Charlou et al.*, 1987, 1988, 1991*a,b*] between 1500 m depth and the seafloor.

In hydrothermal systems, CH_4 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 CH_4 from the mantle via-high temperature hydrothermal systems [*Gold and Soter*, 1982; *Welhan and Craig*, 1982, 1983], and abiogenic seawater-rock interaction involving CH_4 generation through reactions at high temperature (>300-400°C) (such as the Fischer-Tropsch synthesis) in which CO_2, H_2, H_2O, and other hydrocarbon species may participate [*Welhan and Craig*, 1982, 1983; *Welhan*, 1988*a*]. Seafloor hydrothermal discharges exhibit a wide range of CH_4 contents (Table 3) which can be explained in terms of seawater-rock interaction in different geological contexts.

CH_4-enriched plumes were first found along the axes of

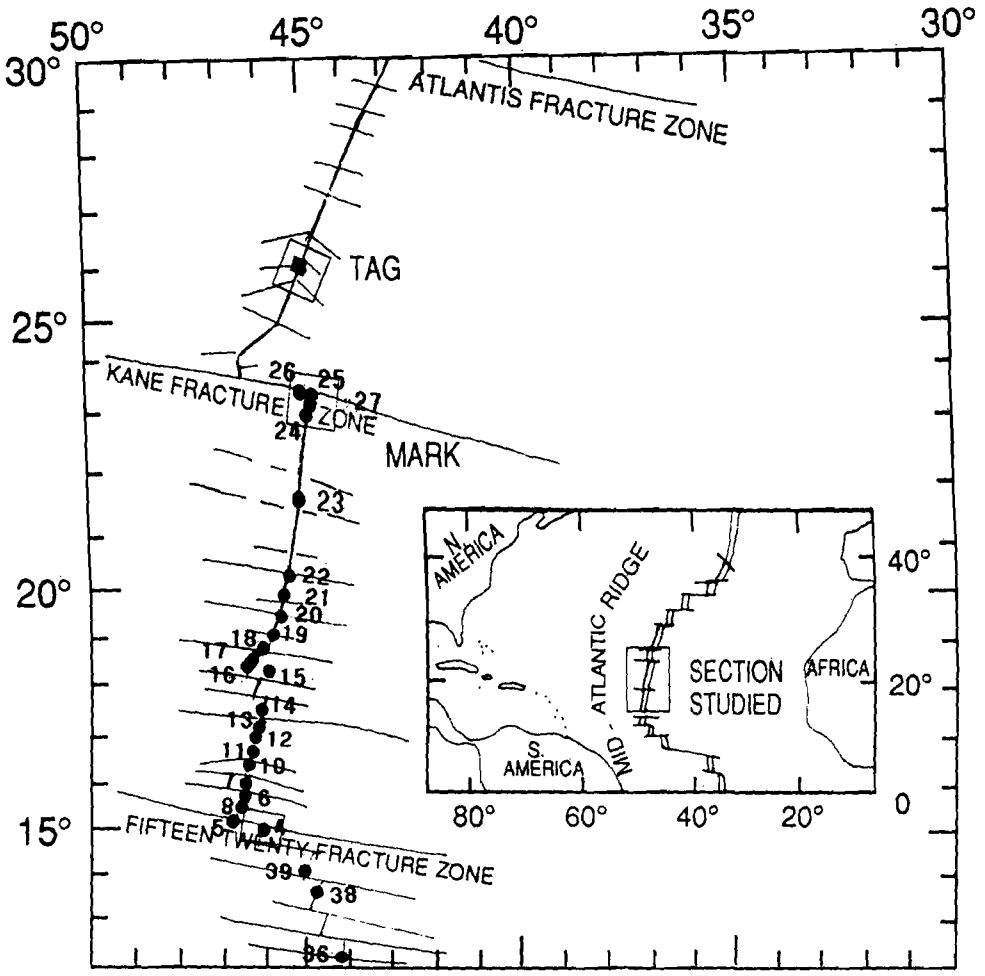

Fig. 1. Regional map of the Mid-Atlantic Ridge between 12°N and 26°N, showing locations of Fifteen Twenty Fracture Zone (FZ), MARK, and TAG areas. Solid circles mark the CTD vertical profiles conducted in the axial area during *Akademik Boris Petrov* (1985) (stations 36, 38, 39) and Ridelente (1988) (stations 4 to 27) cruises. Squares mark known venting sites TAG (26°N) and MARK (23°N) studied during *Atlantis II/ Alvin* cruise in 1990. The eastern intersection of the rift axis with the 15° 20'N FZ 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.*, 1991*a*], in the Guaymas Basin, on the Gorda [*Baker et al.*, 1987*a*], 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 CH_4-enriched water have been detected in back arc basins: the North Fiji basin [*Auzende et al.*, 1988; *Sedwick et al.*, 1990], Mariana [*Horibe et al.*, 1986] and Okinawa [*Kimura et al.*, 1988] troughs, the Lau basin [*Charlou et al.*, 1991*b*], and other basins in the southwest Pacific [*Craig et al.*, 1987*b*; *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 [*Pluger et al.*, 1990]. CH_4 plumes are also clearly identified in the summit crater of the Loihi seamount [*Gamo et al.*, 1987] at the present site of the Hawaian 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 CH_4 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 CH_4 anomalies in the seawater column above some hydrothermal fields along the MAR have been published (12° to 15°N [*Charlou et al.*, 1988, 1991*c*], 23°N [*Jean- Baptiste et al.*, 1991], 26°N [*Charlou et al.*, 1987, 1991*c*].

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 2*a* and Figure 2*a* [*Campbell et al.*, 1988b]. Despite the much greater depth of these vents (3700 m) relative to the EPR depths at 13° or 21°N (2600 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 CH_4 Concentrations and Corresponding Water Depths

Station	Latitude N	Longitude W	Bottom Depth, m	Sample Depth, m	CH4 maximum, nmol/kg	Gelogical Feature
			Akademik Boris Petrov Cruise (1985)			
AK-HY-36	12°24'	44°05'	4800	3541	1,85	Between TFZ and UFZ
AK-HY-38	13°47'	44°59'	3900	2500	0,77	Between 15°FZ and TFZ
AK-HY-39	14'05'	45°01'	3000	2715	1,31	Between 15°FZ and TFZ
			Ridelente Cruise (1988)			
RD-HY-01	15°05.11'	49°22.15'	3030	2000	1,13	off axis station
RD-HY-02	14°46.05'	48°09.57'	3260	2300	0,45	off axis station
RD-HY-03	14°35.63'	46°07.94'	3906	3000	0,50	off axis station
RD-HY-04	14°55.66'	44°55.20'	4005	2897	3,42	Eastern Ridge axis/15°20 FZIntersection
RD-HY-05	15°35.97'	46°33.51'	3994	3101	2,75	Western Ridge axis /15°20 FZIntersection
RD-HY-06	15°48.51'	46°33.66'	3403	3250	3,74	Western Ridge axis/ 15°20 FZIntersection
RD-HY-07	16°08.12'	46°40.33'	4017	3589	1,53	
RD-HY-08	15°44.89'	46°32.98'	3630	3203	2,16	
RD-HY-09	16°01.26'	48°06.56'	4837	2800-4827	0,36	Royal Through
RD-HY-10	16°37.42'	46°30.35'	4230	2498	1,85	
RD-HY-11	16°91.68'	46°27.96'	4724	3400	1,26	
RD-HY-12	17°08.99'	46°29.62'	3905	3200-3800	0,99	
RD-HY-13	17°18.79'	46°26.92'	3655	3496-3655	0,99	
RD-HY-14	17°29.77'	46°27.44'	4300	3300-3500	0,99	
RD-HY-15	18°13.04'	46°25.79'	3847	900-2600	0,27	30 miles east of Ridge axis
RD-HY-16	18°14.44'	46°39.87'	3610	3200-3600	0,77	
RD-HY-17	18°39.53'	46°17.53'	4023	3600	0,90	
RD-HY-18	18°48.30'	46°14.75'	3823	3800	0,77	
RD-HY-19	19°06.81'	46°01.86'	3640	2600-3600	0,45	
RD-HY-20	19°35.50'	45°56.20'	3450	2900	0,72	
RD-HY-21	19°58.54'	45°43.22'	4510	2000-4500	0,32	
RD-HY-22	20°21.53'	45°37.35'	3485	2594	0,77	
RD-HY-23	21°51.35'	45°13.09'	3070	2848	0,90	
RD-HY-24	23°13.52'	44°54.01'	4075	3702	2,34	South MARK site
RD-HY-25	23°24.60'	45°00.00'	4350	3500-3900	0,90	North MARK site
RD-HY-26	23°39.55'	45°10.05'	4300	2500-4300	0,32	KANE FZ
RD-HY-27	23°21.54'	44°56.99'	3680	3392	1,26	500 m south MARK site
			MAR/88 Cruise (NOAA-MAR Program) (1988)			
Cast 01	26°09.1'	44°50.5'	3615	2000	0,59	TAG area
Cast 02	26°08.4'	44°49.6'	3652	2996	0,68	TAG area
Cast 03	26°08.1'	44°49.7'	3387	3305	8,33	TAG area
Cast 06	26°08.1'	44°49.4'	3732	3438	9,05	TAG area
Cast 07	26°08.3'	44°49.8'	3691	3340	8,37	TAG area
Cast 08	26°09.4'	44°48.8'	3480	3412	9,45	TAG area
Cast 09	26°07.8'	44°50.8'	3843	3263	9,00	TAG area
Cast 10	14°56.3'	44°53.9'	3757	2502	2,70	lower east wall
Cast 11	14°55.0'	44°53.9'	2964	2900	2,66	base of east wall
Cast 12	14°55.0'	44°54.1'	2923	2603	3,56	lower east wall
Cast 13	14°54.1'	44°54.6'	3554	2960	4,77	lower east wall
Cast 14	15°06.5'	44°55.2'	3550	2997	17,78	east margin to center of dome
Cast 15	15°05.7'	44°57.0'	3475	2803	15,62	east margin to center of dome
Cast 16	15°06.7'	44°56.9'	3029	2591	2,12	north margin to center of dome
Cast 17	14°56.1'	44°51.5	2773	2500	5,27	south to north transect on east wall
Cast 18	14°54.0'	44°53.4'	2798	2704	4,82	east to west transect from east wall to ridge axis

TFZ and UFZ are Marathon (12°N60'N) and Mercurius (12°20'N) Fracture Zones, respectively.

TABLE 2*a*.. MAR/90 (*Atlantis II/Alvin* Cruise): CH_4 in the Neutrally Buoyant Plume Above TAG

Depth, m	Bottle	$Si(OH)_4$, µmol/kg	Mn, nmol/kg	CH_4, nmol/kg
3490	3	4.0	4.1	7.56
3405	4	3.9	3.5	3.92
3343	5	4.2	3.5	4.14
(leaks)	6	(5)	(1.5)	1.9
3341	11	3.8	2.5	3.15
3250	7	4.0	5.4	4.86
3200	8	3.5	0.8	0.99
3150	9	3.5	0.2	0.77
3098	10	3.5	0.2	0.63

Bottom depth of 3650 m.

TABLE 2*b*. MAR/90 (*Atlantis II/Alvin* Cruise): CH_4 in Buoyant Plumes Above TAG and MARK Sites

Dive	Bottle	$Si(OH)_4$ µmol/kg	Mn, nmol/kg	Li, µmol/kg	CH_4, nmol/kg
		TAG *Buoyant Plume*			
2182	1	95	1550	26.4	192.6
2182	5	59	800	26.1	67.8
2182	9	52	490	25.5	57
2182	11	70	930	26.5	98.1
2185	1	63	820	26.4	64.4
2185	9	223	7000	28.6	672.7
		MARK *Buoyant Plume*			
2192	1	70	740	27.8	54.9
2192	9	219	3850	31.8	326.8
2192	12	151	2240	29.2	300

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

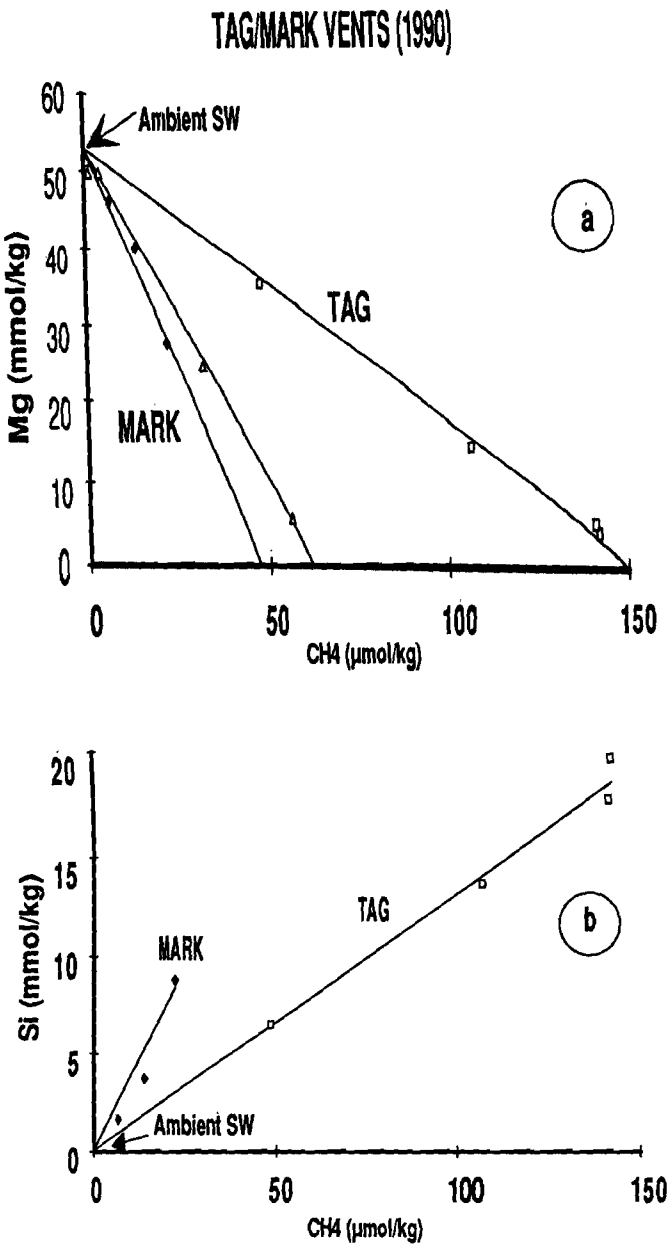

Fig. 2. MAR/90 (*Atlantis II/Alvin* cruise). (*a*) CH_4 end-members calculated for a zero Mg concentration in TAG (q) (150 µmol/kg) and MARK (n) (48 µmol/kg) fluids. CH4 endmember (62 µmol/kg) obtained in fluids sampled during the French Hydrosnake (1988) cruise above MARK (D) are presented for comparison. (*b*) CH_4/Si correlations found in the same TAG and MARK vent fluids.

TABLE 2*c*.MAR/90 (*Atlantis II/Alvin* Cruise): CH_4 in Hot Fluids From TAG and MARK Sites

Dive	Bottle	Temperature °C	Mg, mmol/kg	*p*H	$Si(OH)_4$, mmol/kg	H_2S, mmol/kg	CH_4*, µmol/kg	CH_4**, µmol/kg
				TAG *Vents*				
B.S.2179	5C	364	2.9	3.29	19.75	0.5	143.1	150
B.S.2186	3C	360	3.4	3.46	17.90	0.5	142.2	151
W.S.2187	3C	300	14.4	3.05	13.70	0.1	107.5	146
W.S.2191	2C	300	35	4.79	6.50	0.1	49	143
				MARK *Vents*				
B.S.2192	2C	337	45.7	0.6	1.60	0.0	6.7	48.7
B.S.2192	7C	92	40.6	0.6	3.65	0.1	14	59.4
B.S.2194	4C	352	27.5	0.5	8.80	0.5	22.5	46.4

Bottom water samples: Si, 35,5 µmol/kg; Mn, 0,20 nmol/kg; Mg, 53 mmol/kg; CH_4, 0,40 nmol/kg.

* concentrations measured in samples,

** End-members calculated by extrapolation for individual vents to zero magnesium. Chemical data, except CH_4, are from A. Campbell (personal communication, 1990).

concentrations are similar to the extrapolated 1986 data [*Edmond et al.*, 1990]. A large CH_4 content (endmember of 150 μmol/kg) was measured in the 1990 TAG vent samples (Table 2*a*). CH_4 concentrations varying from 54 to 670 nmol/kg were found in the buoyant plume, while these values dropped to 0.9 to 8.0 nmol/kg in the neutrally buoyant part of the plume (Table 2*b*). A good correlation was observed in hot fluids between CH_4 and silica with a Si/CH_4 ratio of 130 mol/mol. This ratio was found to be 6 and 200 times greater respectively in buoyant waters and waters of the effluent layer in the same area (Figure 2*b*). This CH_4 enrichment in fluids explains the CH_4 anomalies found in samples collected in CTD tows conducted during MAR/88 cruise in this area. The plume was clearly identified between 3200 m and 3500 m depth. Globally CH_4 anomalies (up to 9 nmol/kg) are correlated with temperature anomalies [*Rona et al.*, 1986], excess of dissolved Mn [*Klinkhammer et al.*, 1985; *Charlou et al.*, 1991c)], nephelometry anomalies [*Nelsen et al.*, 1986/87, 1988], and particulate iron and suspended matter [*Trefry et al.*, 1985; *Trocine and Trefry*, 1988]. Specifically, three plumes were tentatively identified in this area: the one associated with the known source [*Rona et al.*, 1986], a southern plume, and a smaller, less well 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 CH_4 end-member calculated in high temperature (337°-352°C) vent (Table 2*c*) samples showed values of 46 to 49 μmol/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 CH_4 analysis on shore. CH_4 and He gas concentrations are positively correlated with Mg contents. A mixing line calculation gives a CH_4 end-member of 62 μmol/kg (Figure 2a) corresponding to 10^6 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 CH_4 was analyzed by the stripping/trapping method on shore. CH_4 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 CH_4 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 CH_4 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. CH_4 concentrations found in Snakepit fluids are uniform and of the same order of magnitude as those found in the 21°N [*Welhan and Craig*, 1979, 1983] or 13°N [*Merlivat et al.*, 1987] fluids on the EPR. CH_4 concentrations varying from 55 to 326 nmol/kg were observed in the buoyant plume immediately above the vents (Table 2*b*).

During the Ridelente cruise in 1988, four CTD/casts were conducted in the MARK area (Figure 4). A typical CH_4 reference

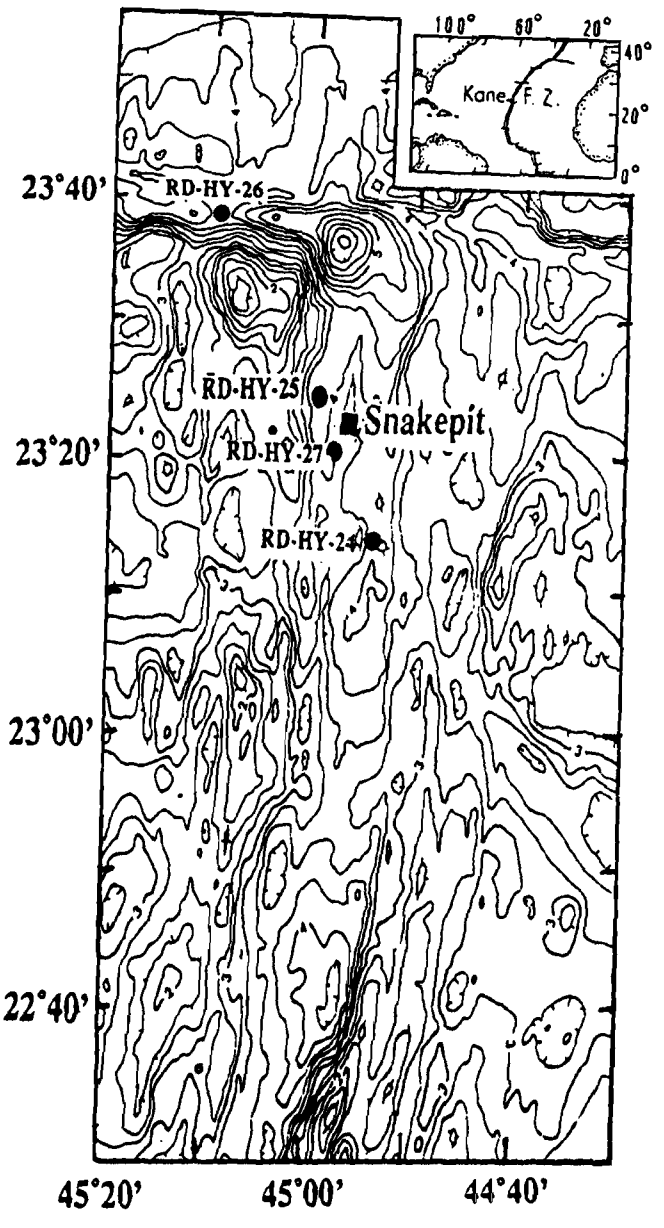

Fig. 3. Sea Beam map of the Snakepit hydrothermal area, south of the intersection of the MAR rift valley and the Kane FZ [*Detrick et al.*, 1984]. The square indicates the Snakepit hydrothermal field (23°22.08'N-44°57.00'W). The Snakepit field is on the top of a large volcanic ridge in the axial portion of the rift valley. The ridge is 400 m-600 m high and about 40 km in length. The vent field consists of a wide area (>40,000 m^2) of dark hydrothermal deposits, numerous chimneys and mounds, and high temperature black smokers on a small terrace of glassy pillows at 3500 m depth in the middle of the neovolcanic zone [*Karson et al.*, 1987]. Hy-24, 25, 26, 27 are CTD/casts conducted in this area during the Ridelente cruise in 1988. RD-Hy-26 was conducted in Kane FZ.

profile is found at RD-HY-26 located at 23°39.55'N in the Kane FZ. RD-HY-25, just north of the MARK site, shows a CH_4 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 CH_4 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

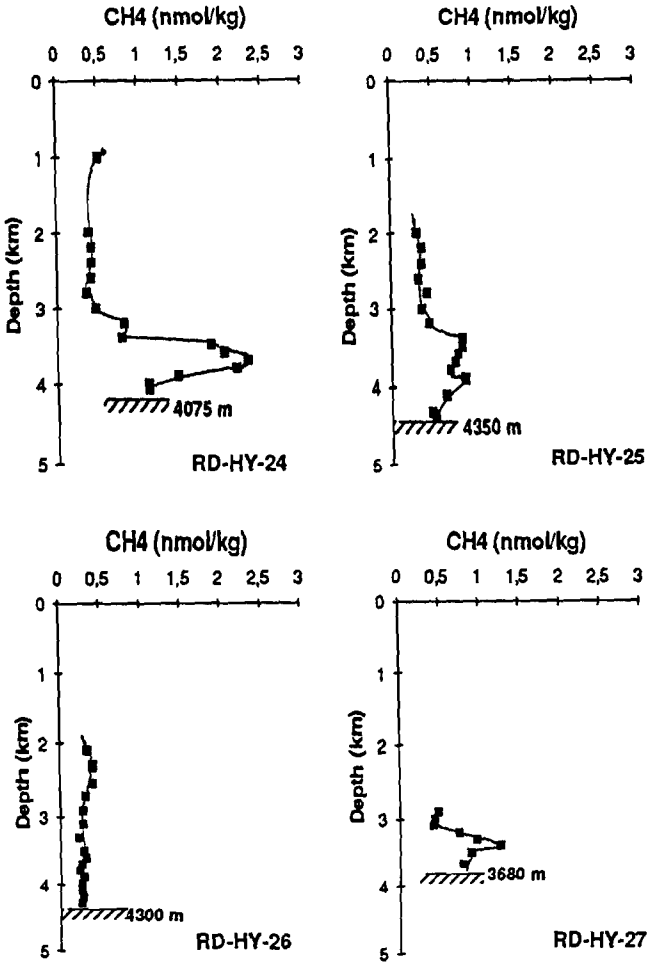

Fig. 4. CH_4 concentration versus depth at stations RD-H-24, 25, 26 and 27 conducted during the Ridelente cruise (1988), and around MARK area (23°22.08'N-44°57.00'W). RD-Hy-26 conducted in Kane FZ. shows a CH_4 profile near the background.

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, Oceanographer, 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.* [1990*ab*, this issue].

During the Ridelente cruise in 1988, CH_4 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 CH_4 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], CH_4 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 CH_4 concentration (up to 8.9 nmol/kg) and elevated nephelometry signals. Plumes of a different composition were identified at 15°N with surprisingly high CH_4 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, CH_4 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°59'W, from the eastern margin (water depth of 3400 m) to the dome top (water depth of 2500 m) exhibited an abrupt increase in CH_4 (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 CH_4 (up to 6.7 nmol/kg) over the center. Relatively high CH_4 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 CH_4 with lesser TDM enrichment. The CH_4 anomalies are clearly defined around 2500 and 3000 m depths, giving a typical bimodal shape for CH_4 profiles in this area. This characteristic was never observed on CH_4 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 CH_4 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 CH_4 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 CH_4 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 CH_4 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 CH_4 profiles with a first strong anomaly (1.83 nmol/kg) around 2500 m, a second smaller anomaly (1.16 nmol/kg) around 3200 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 CH_4 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 CH_4 = 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), CH_4 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 CH_4 profile near background, even though a slight anomaly can be detected at around 3000 m depth. Farther north, CH_4 anomalies (0.89 nmol/kg) are again clearly defined on RD-HY-22 and 23 between

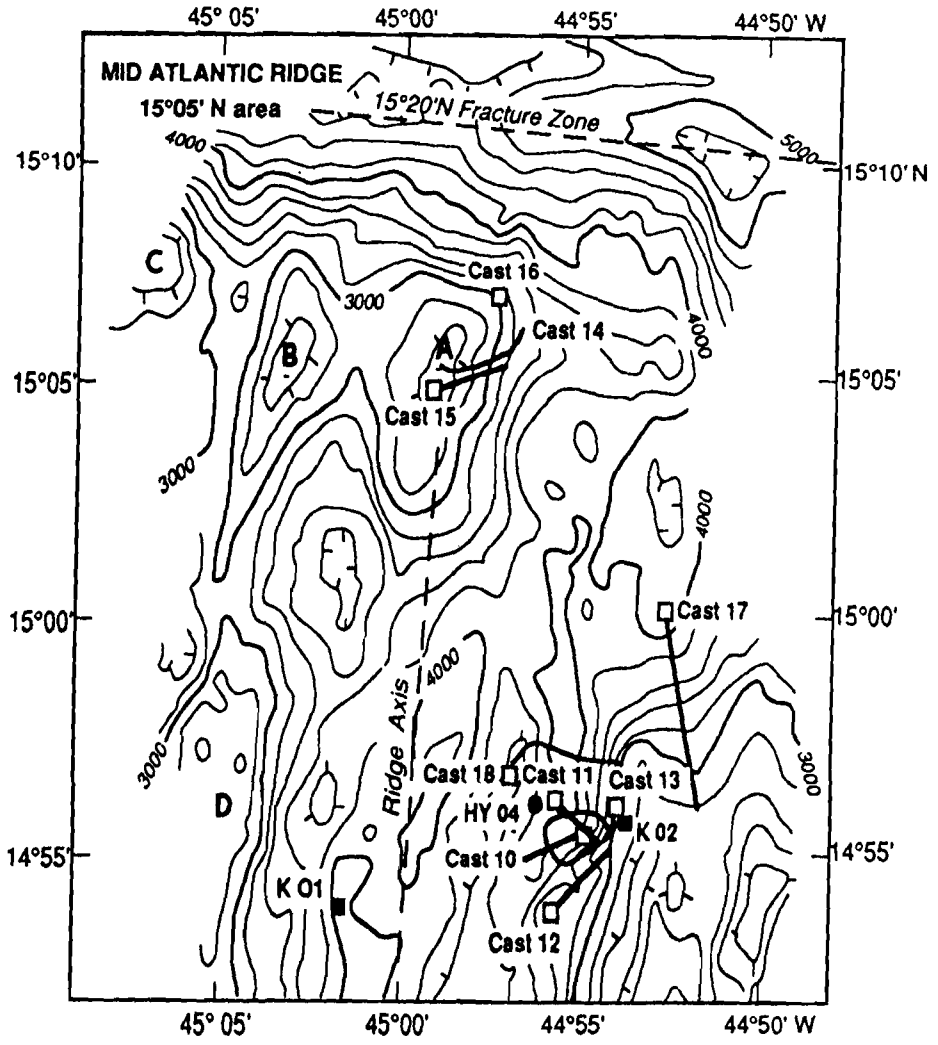

Fig. 5. Water column stations conducted on the east wall and axial dome close to the 15°20'N FZ./Ridge axis intersection during MAR/88 cruise (1988). The Sea Beam map was established during the Ridelente cruise (1988). The solid lines represent the CTD tracks and the open squares are the upcasts at the end of tows. K01 (14°53.8'N-45°01.6'W) and K02 (14°55.0'N-44°90.0'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 serpentinite 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 CH_4 profiles. Except for these two profiles, all other profiles show significant but variable CH_4 anomalies along this MAR section. In addition, it can be observed that a CH_4 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 CH_4 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 CH_4 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 CH_4 anomaly at one station (HY-36), integrated over more than 1000 m, reflects a large CH_4 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 (2╥-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

CH_4 Plume Geometry on the MAR (Figure 8)

CH_4 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 CH_4 plumes rising up to 300 m above the seafloor in the rift valley. However, the various CH_4 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].

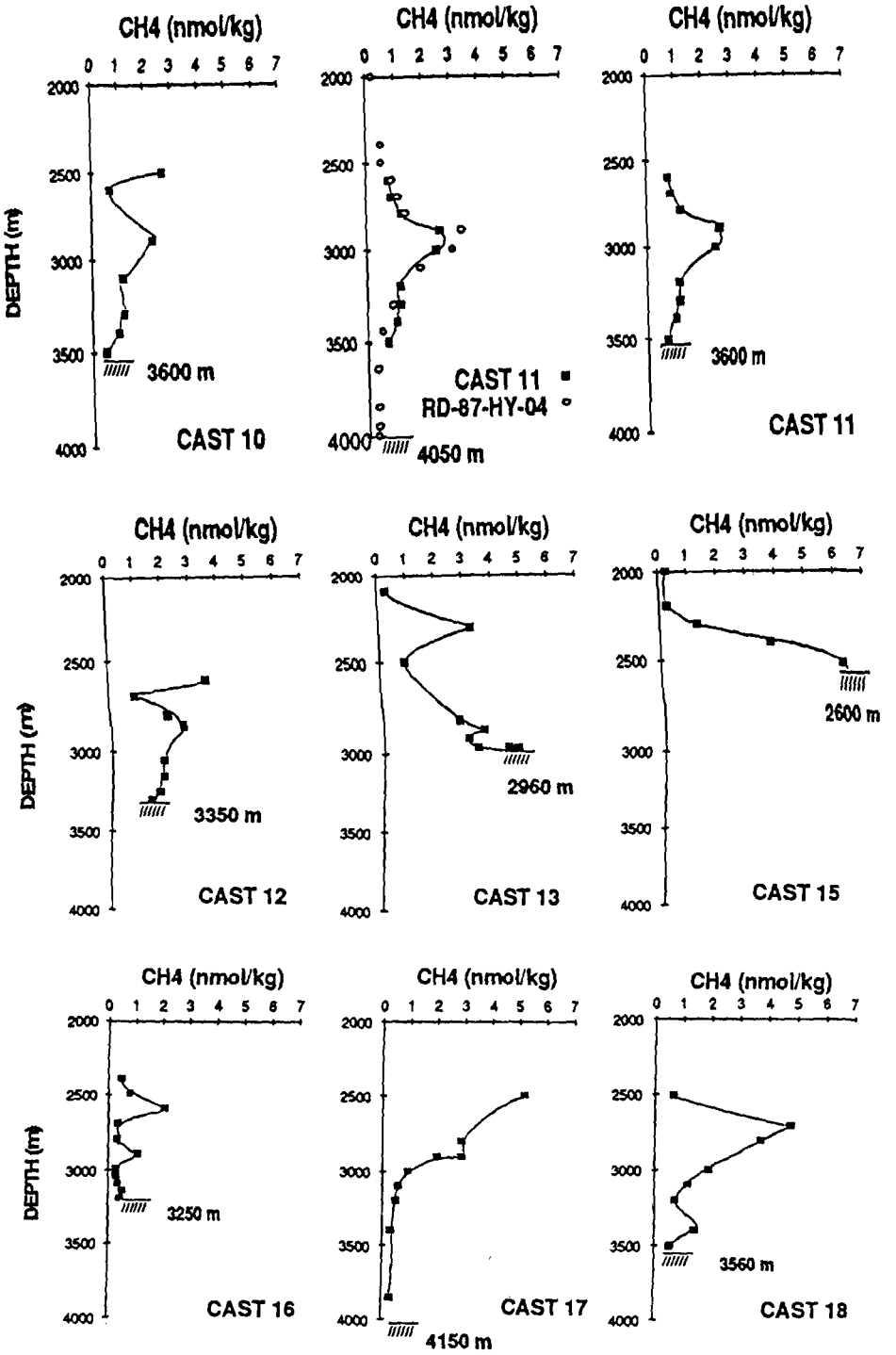

Fig. 6. Vertical profiles of CH_4 for stations in the 15°N area. The CH_4 profile (RD-HY-04) (open circles) obtained during the Ridelente cruise (1988) is superimposed on the CH_4 profile of cast 11 (solid circles) obtained during MAR/88 cruise to show the good concordance between the 1985 and 1988 profiles. CH_4 concentrations are elevated (up to 6.7 nmol/kg) in cast 15 conducted just above dome A (Figure 5). CH_4 plumes show maxima CH_4 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 CH_4, He or Mn plumes [*Charlou et al.*, 1991a]. Typical reference profiles found on the MAR and the EPR are presented respectively on Figures 8*a* and 8*b*. Figure 8*c* shows the CH4 profile observed at HF-19 station (Hydrofast cruise) [*Charlou et al.*, 1991*a*] 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 8*d*). The different shapes of the CH_4 plume observed along the MAR between 12° and 23°N are shown in Figures 8*e* and 8*h*

the topography of ridges. The vertical CH_4 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 8*c*). 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; *Nelsen et al.*, 1986]

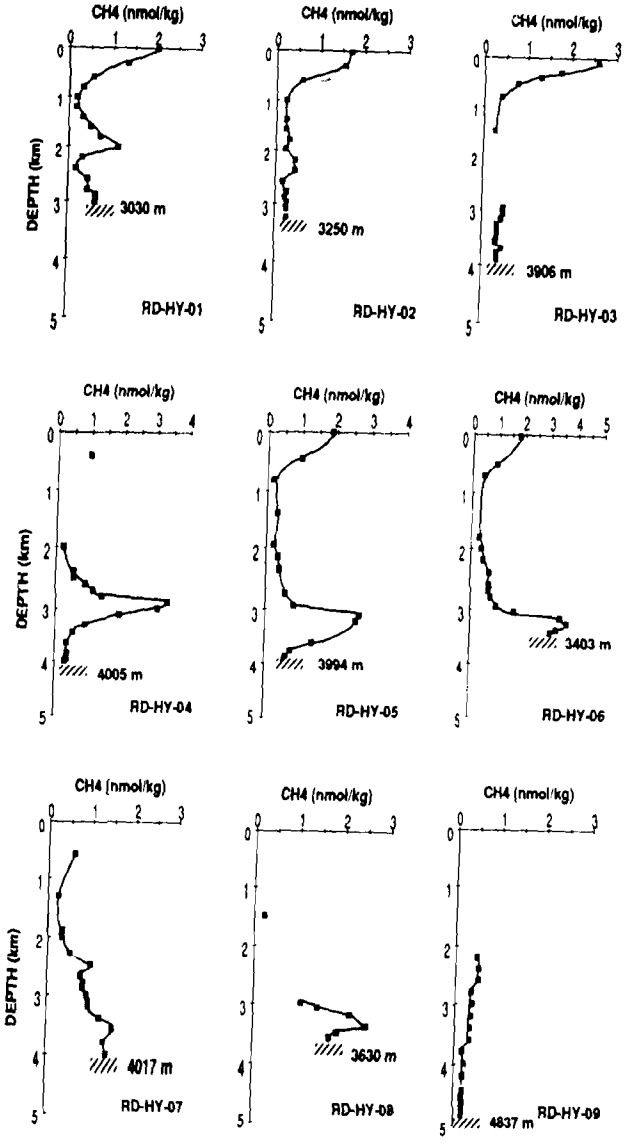

Fig. 7. CH_4 versus depth for stations sampled between 12° and 23°N during the Ridelente cruise (1988).

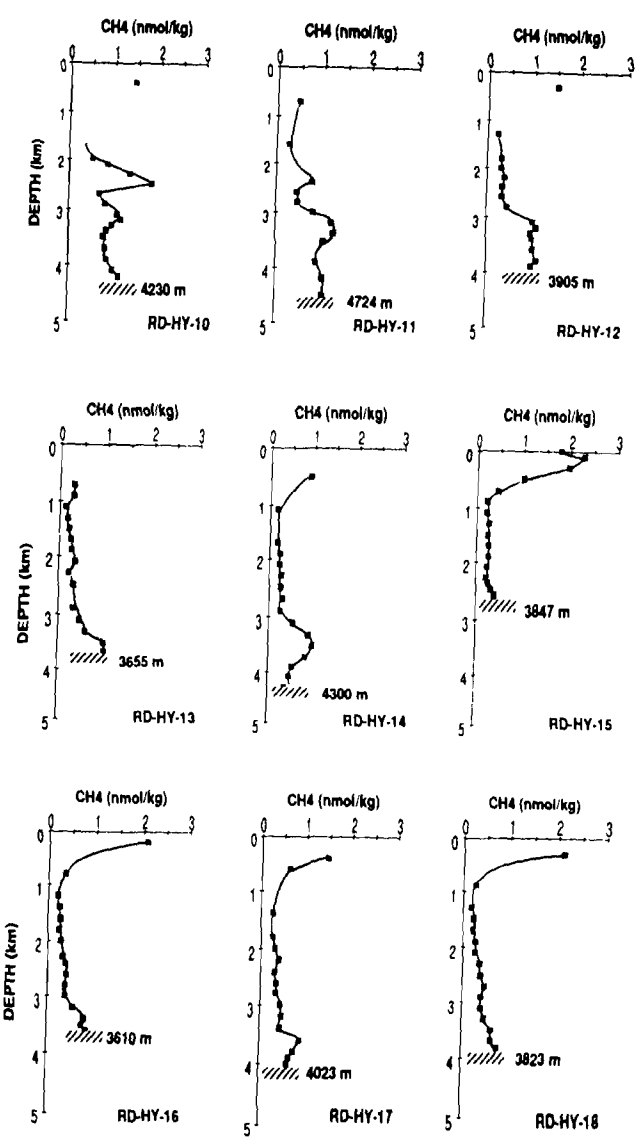

Fig. 7 (continued).

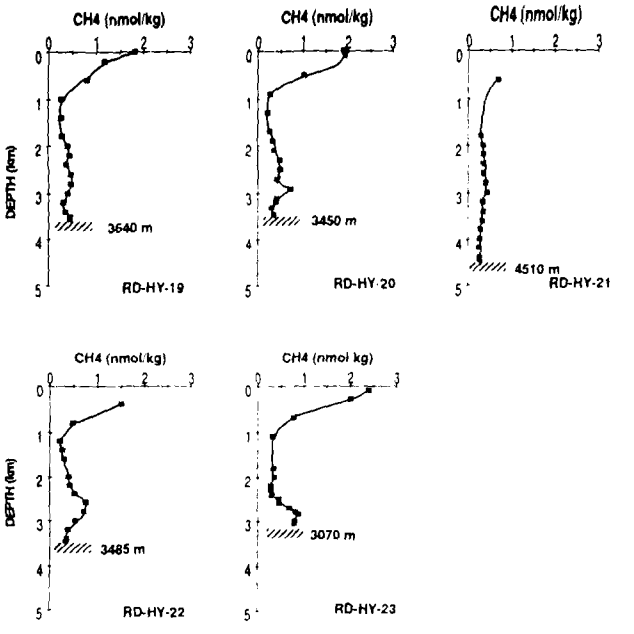

Fig. 7 (continued).

particles [*German et al.*, this issue] emitted from the inner floor and the walls of the rift valley cannot be dispersed widely across

of the abyssal landscape. Only the CH_4 plumes emitted on the tops of the rift valley walls can be disseminated outside the rift valley (see RD-HY-10). The CH_4 anomalies observed at different levels in a 1000-m layer above the seafloor of the MAR (Figures 8*e*, 8*f*, 8*g*, and 8*h*) 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). CH_4 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 CH_4 degassing decreases progressively from the inner floor to the top of the rift mountains. In addition, no CH_4 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 CH_4 degassing. On the EPR, the fluids extract light volatile elements such as H_2, He, and CH_4 directly by leaching hot fresh basalt where these gases are present in great quantities. CO_2 and H_2S in the 350°C fluids are in the range of 5-10 mmol/kg, while CH_4 and H_2 have been measured up to 0.1 and 2 mmol/kg [*Kim et al.*, 1884;*Welhan and*

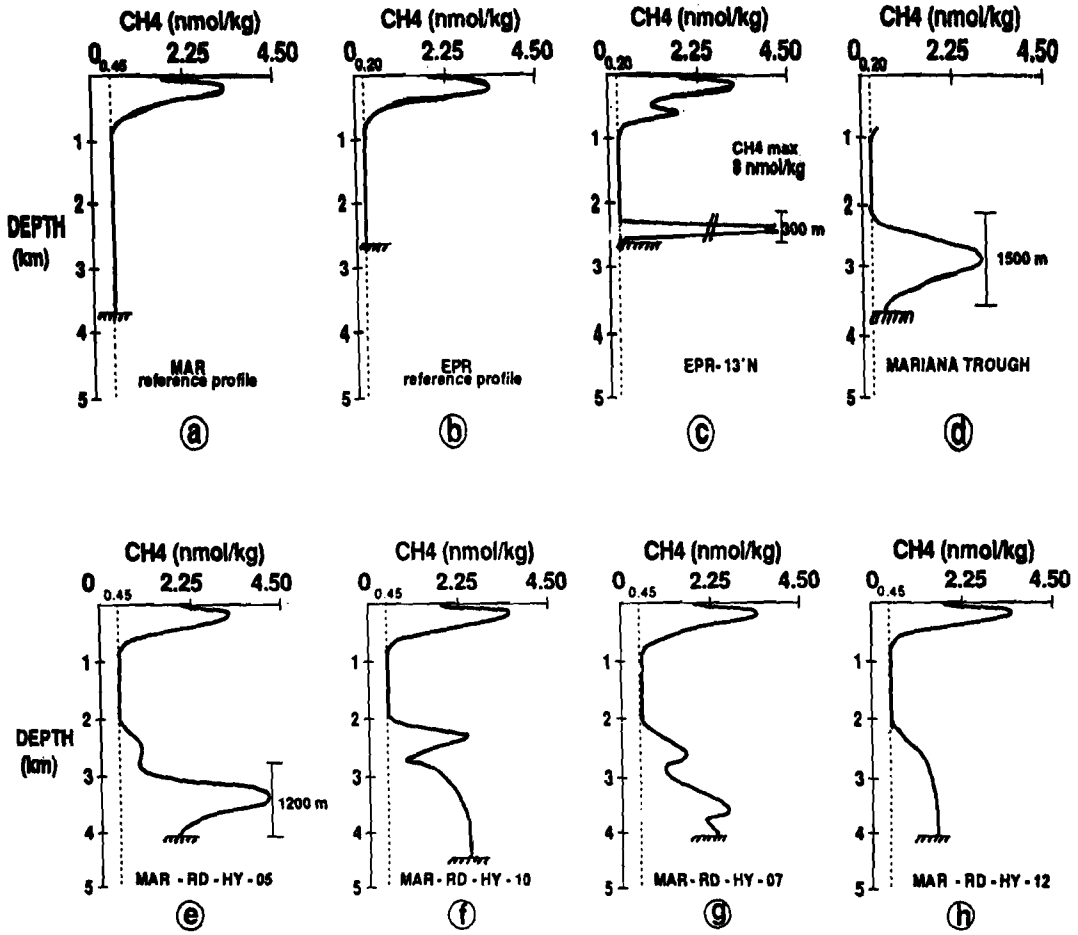

Fig. 8. CH_4 plume geometry observed along the Mid-Atlantic Ridge. (*a*) Typical CH_4 depth profile in the Atlantic Ocean without any detected anomaly. Station HY-14: 13°20.87'S-14°05.51'W; depth: 3570 m [after *Charlou et al.*, 1987]. (*b*) CH_4 depth profile at a control station in the Pacific Ocean [after *Charlou et al.*, 1991*a*]. (*c*) Hydrothermal CH_4 plume observed in the 300 m layer above the seafloor at 13°N on the East Pacific Rise [after *Charlou et al.*, 1991*b*]; a biological peak is observed in the 500-700 m layer in this denitrification area (J.L. Charlou personal communication,1990). (*d*) CH_4 plume in the Marianna back arc spreading center [after Horibe et al., 1986]. (*e*) MAR CH_4 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 CH_4 degassing on the top of rift mountains around 2500m depth) and regular increase to the seafloor (station RD-HY-10 of the Ridelente cruise, (this work)). (*g*) Profile showing two clearly defined CH_4 plumes (stations RD-HY-07, 11 of the Ridelente cruise, (this work)]. (*h*) CH_4 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, CH_4 has a clearly thermogenic origin as indicated by $C_1/(C_2\text{-}C_5)$ 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 $CH_4/^3He$ ratio of 2.6×10^6 found in Snakepit fluids [*Jean-Baptiste et al.*, 1991] is similar to the $CH_4/^3He$ ratio found in MAR basalt glasses (0.7×10^6) and in MAR volcanic "popping rocks" (2.1×10^6) [*Welhan and Craig*, 1983; *Pineau et al.*, 1976], suggesting a nonbiogenic origin of CH_4 in this area. The CH_4 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 CO_2 and H_2.

TDM and CH_4 in the Serpentinization Process: TDM/CH_4 Covariation

Some discrepancies have been shown to exist between total dissolvable manganese (TDM) and CH_4 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/CH_4 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 CH_4 concentrations and nephels and CH_4 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 CH_4, 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/CH

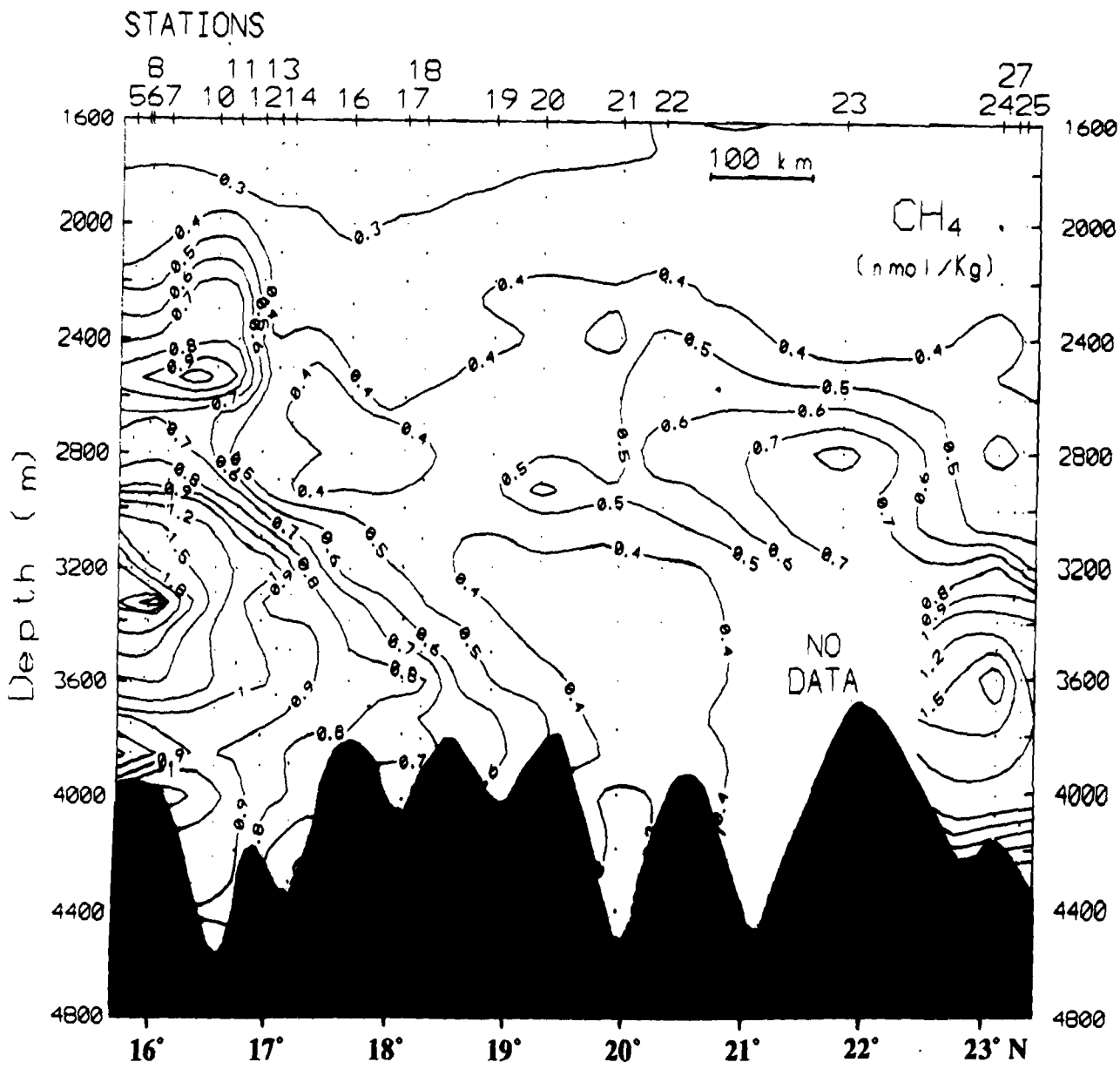

Fig. 9. Methane fields between 1600 m and the seafloor along the section 15°36'N / 23°N of the MAR. CH_4 plumes in the inner floor are clearly identified near the 15°20'N and Kane FZ. A CH_4 plume emitted at the top of rift mountains (2500 m) is defined around 16°30'N. Sample depths are indicated by dots (bottle data). The bathymetry of the ridge axis is schematic and very expanded.

TABLE 3. CH_4 End-members in Hydrothermal Fluids Compared to CH_4 Content in MORB Glasses

Location	CH_4 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	*Lilley et al.* [1983]
Guaymas Basin	12150 - 16650	*Welhan and Lupton* [1987]
southern, JDFR	81 - 117	*Evans et al.* [1988]
Axial Seamount,JDFR	25	*Butterfield et al.* [1990]
Endeavour, JDFR	504 - 1413	*Lilley 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]

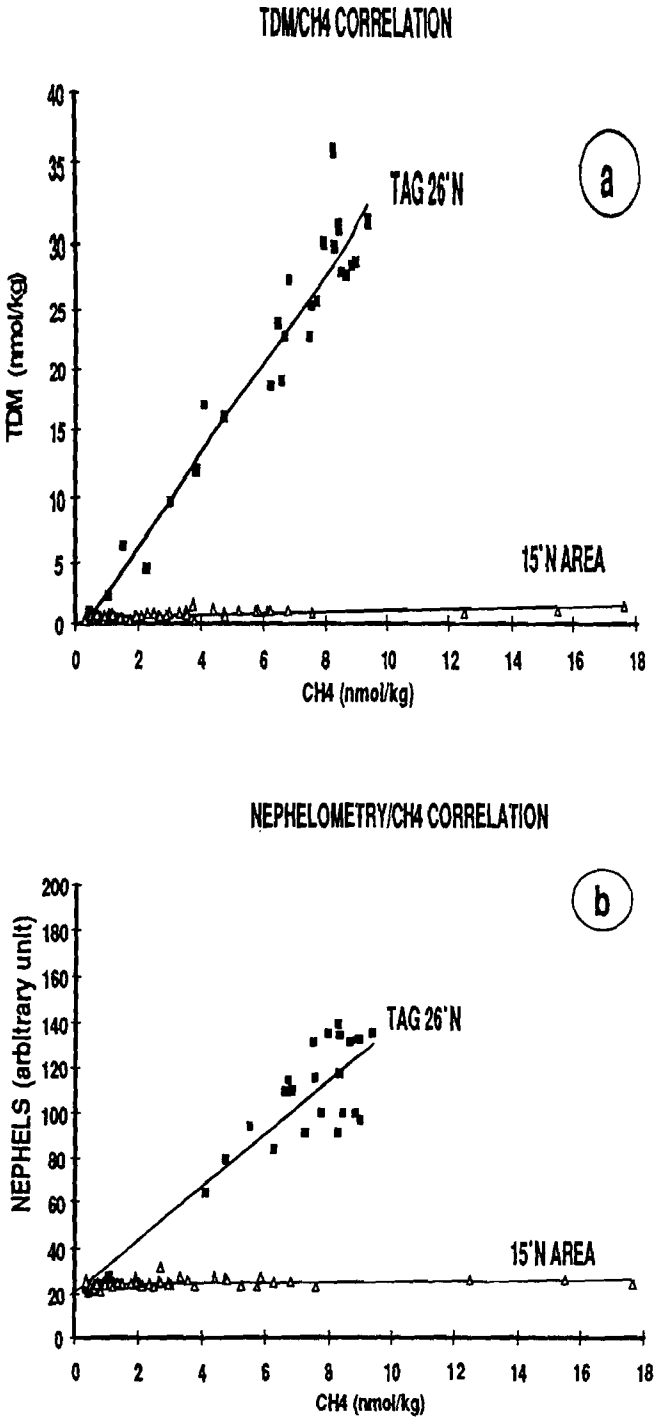

Fig. 10. Evidence of different hydrothermal processes from TDM/CH_4 and Nephel/CH_4 ratios at TAG (26°N) and 15°N area [*Charlou et al.*, 1991*c*; *Rona et al.*, 1992]. Nephels measurements are from *T. Nelsen* (NOAA-Miami) and TDM measurements are from *P. Appriou* (University of Brest, France). These data were obtained during NOAA MAR/88 cruise (1988).

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 CH_4 concentration on the MAR (this work) is similar to that encountered elsewhere. The significant difference in TDM/CH_4 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.*, 1990*a*,*b*, this issue; *Charlou et al.*, 1991*a*,*c*]. The particularly low TDM/CH_4 ratio found in plumes over the 15°05'N area on the MAR is probably a 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 CH_4 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 [*Mottl 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 (*p*H=12.5) enriched in CH_4 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 *p*H solutions with high TDM (up to 1 mmol/kg) and CH_4 (up to 144 µmol/kg) concentrations (Table 3). In the 15°N area, the interaction between seawater and ultramafic rocks may give basic *p*H solutions which are highly enriched in CH_4, 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 *p*H fluids in the hydrothermal/serpentinization process.

A direct mantle origin and a serpentinization origin can both be compatible to explain the high CH_4 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 CH_4. The ultramafic rock-seawater interaction as observed on the axial serpentinite dome (15°05'N) generates solutions with a high CH_4 content, probably associated with H_2 and CO_2 gases. Therefore, if the major element chemistry of the peridotite is generally not significantly modified by serpentinization at temperatures below 500°C, serpentinization in CO_2-rich fluids at 300°C, 500 bars results in the generation of H_2 and in partial conversion of CO_2 to hydrocarbons [*Janecky and Seyfried*, 1986; *Abrajano et al.*, 1988; *Szatmari*, 1989]. In addition, H_2 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 H_2, formed by the reduction of H_2O 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 H_2 enhance-

hydrocarbon generation by hydrogenation. The reduction of CO_2 through the Fischer-Tropsch synthesis produces CH_4 and unsaturated hydrocarbons. In conclusion, conditions under which CH_4 can be produced occur where there are adequate supplies of carbon and a suitable reductant (such as H_2, Fe^{2+} or Fe^0). These reduced gas occurrences are closely associated with mafic-ultramafic rocks. The presence of H_2-CH_4 gas seeps in serpentinized mafic-ultramafic rocks suggests a possible correlation between reduced gas formation and serpentinization. Magnetite, serpentine, brucite, and H_2 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. CO_2, CO, CH_4) 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 CO_2 [*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

CH_4 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 CH_4 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.*, 1990*a*,b, this issue]. These diapirs form dome-shaped features in the rift valley and adjacent fracture zone. CH_4 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 diapiric 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

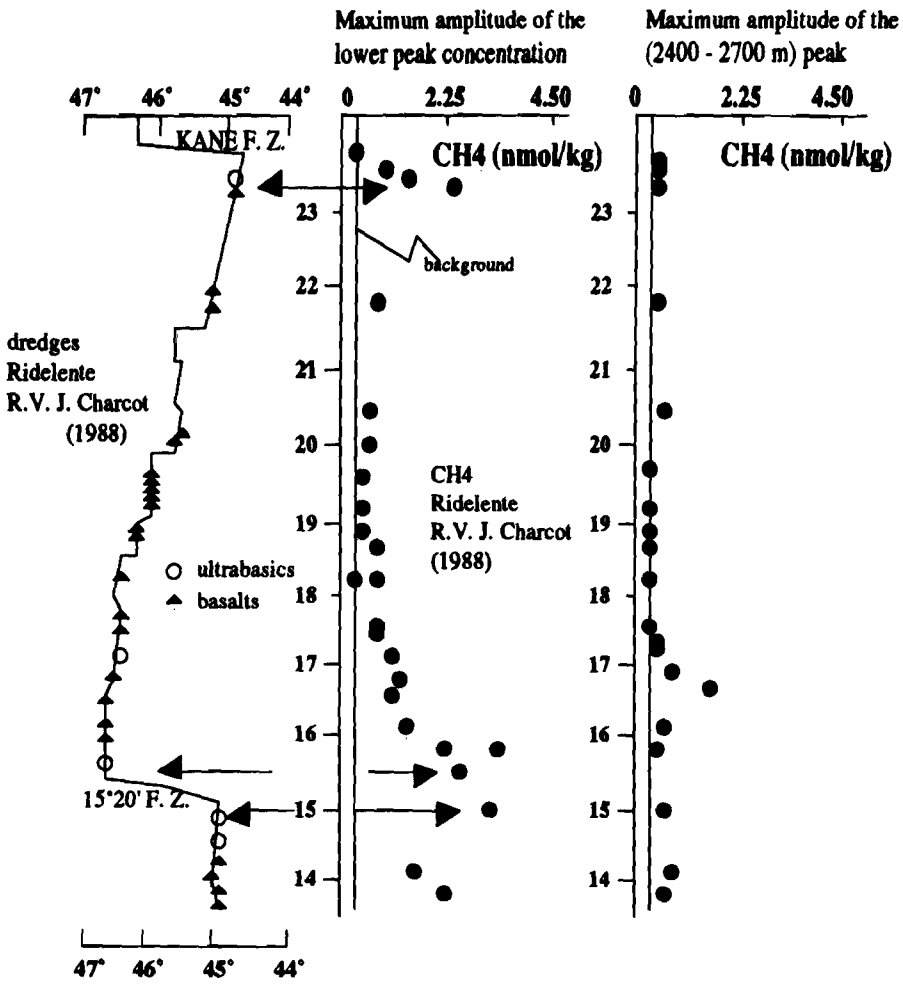

Fig. 11. CH_4 variation between 14°N and 23°N along the MAR. The schematic ridge axis (after *H.D. Needham*, unpublished data, 1987) is represented on the left side. Solid triangles and open circles show respectively basalts and ultramafic rocks collected in dredges conducted in the CTD/cast areas. Solid circles represent maximum CH_4 concentration measured on each profile in two seawater layers: CH_4 max.ima in the (2700-m bottom) layer (lower peak) in the middle, and CH_4 maxima in the 2400-2700 m layer (upper peak) on the right side of the figure. CH_4 background is 0.36 nmol/kg in Atlantic deep waters.

different tectonic settings along the Mid Atlantic Ridge [*Rona et al.*, 1992].

SUMMARY AND CONCLUSIONS

In spite of its nonconservative property, CH_4 is a good tracer of hydrothermal activity along mid-oceanic ridges. CH_4 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 CH_4 plumes. These CH_4 plumes have maxima above the two vent fields (TAG and MARK) known at the present time. The shape of CH_4 profiles clearly shows the water depth of sources, with CH_4 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 CH_4 and other chemical tracers (i.e., TDM/CH_4) contribute to determination of the distribution, type, and chemical composition of vents along a spreading ridge segment and may provide information on the subseafloor processes involved in mantle structure and mechanisms which form the ridges. CH_4 and TDM data obtained along the MAR show that different TDM/CH_4 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 subseafloor processes along mid-oceanic ridges. The high TDM/CH_4 ratio found above TAG and MARK areas is indicative of basalt-seawater interaction, while at 15°05N the low TDM/CH_4 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 downnwelling of seawater and serpentinization of lower crustal and upper mantle ultramafic rocks. CH_4 investigations reveal and confirm the association between hydrothermal activity, serpentinization, diapirism and mantle degassing along the Mid-Atlantic Ridge.

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