

# 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 CH<sub>4</sub>-rich water column plumes. The vertical distribution of CH<sub>4</sub> at stations located every 20-40 km is presented along this 1200-km-long section of the MAR. CH<sub>4</sub> venting is clearly demonstrated. CH<sub>4</sub>-enriched fluids rise from vents as plumes; spreading is confined to the axial valley due to the topography of the MAR. CH<sub>4</sub> 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 CH<sub>4</sub> 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. CH<sub>4</sub> 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 CH<sub>4</sub> is known to be unstable with respect to oxidation by dissolved oxygen, and in spite of its microbial oxidation in plumes, these results confirm CH<sub>4</sub> 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, CH<sub>4</sub> 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 CH<sub>4</sub> tracer with total dissolvable manganese (TDM) tracer in plumes allows us to differentiate seafloor hydrothermal processes. The high TDM/CH<sub>4</sub> found above TAG and MARK areas is indicative of basalt-seawater interaction, while at 15°N the low TDM/CH<sub>4</sub> provides evidence of fluid circulation in ultrabasic rocks. CH<sub>4</sub> 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 seafloor 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.*, 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; Charlou *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 [Charlou *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 [Charlou *et al.*, 1991a]. 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<sub>4</sub> [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 <sup>3</sup>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 CH<sub>4</sub>, H<sub>2</sub>, Mn, and particles [Kadko *et al.*, 1990]. Microbial CH<sub>4</sub> 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<sub>4</sub> not to be a conservative tracer. Although CH<sub>4</sub> 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<sub>4</sub> 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, CH<sub>4</sub> 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; Pluger *et al.*, 1990].

In the Atlantic Ocean, CH<sub>4</sub> 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<sub>4</sub> in the seawater column along the Mid-Atlantic Ridge axis. Evidence of CH<sub>4</sub> 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 *Nadir* with the submarine *Nautille* 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<sub>4</sub> 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<sub>4</sub> equipment was set up in a portable clean air-conditioned van, permitting CH<sub>4</sub> 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<sub>2</sub>-C<sub>4</sub> hydrocarbons and activated charcoal for trapping CH<sub>4</sub> and CO, respectively. For this study, only CH<sub>4</sub> was analyzed. By raising the trap temperature, the CH<sub>4</sub> 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<sub>4</sub> standards (2 ppmv  $\pm$  2% and 10 ppmv  $\pm$  2% in pure helium) were injected through calibrated loops to the detector at appropriate time intervals. Known amounts of CH<sub>4</sub> 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<sub>4</sub> per kilogram of seawater. Taking into account the precision of the calibration, blanks correction, and reproducibility, the precision was  $\pm$  3% within a CH<sub>4</sub> concentration range of 0.22-18 nmol/kg.

#### CH<sub>4</sub> ANOMALIES IN DEEP WATER AT SPREADING AXES

In oceanic regions unaffected by hydrothermal inputs, deep waters are CH<sub>4</sub> undersaturated due to in situ consumption [Scranton and Brewer, 1978], and CH<sub>4</sub> concentrations decrease with depth to respective 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, 1991a,b] between 1500 m depth and the seafloor.

In hydrothermal systems, CH<sub>4</sub> 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<sub>4</sub> from the mantle via high temperature hydrothermal systems [Gold and Soter, 1982; Welhan and Craig, 1982, 1983], and abiogenic seawater-rock interaction involving CH<sub>4</sub> generation through reactions at high temperature (>300-400°C) (such as the Fischer-Tropsch synthesis) in which CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, and other hydrocarbon species may participate [Welhan and Craig, 1982, 1983; Welhan, 1988a]. Seafloor hydrothermal discharges exhibit a wide range of CH<sub>4</sub> contents (Table 3) which can be explained in terms of seawater-rock interaction in different geological contexts.

CH<sub>4</sub>-enriched plumes were first found along the axes of

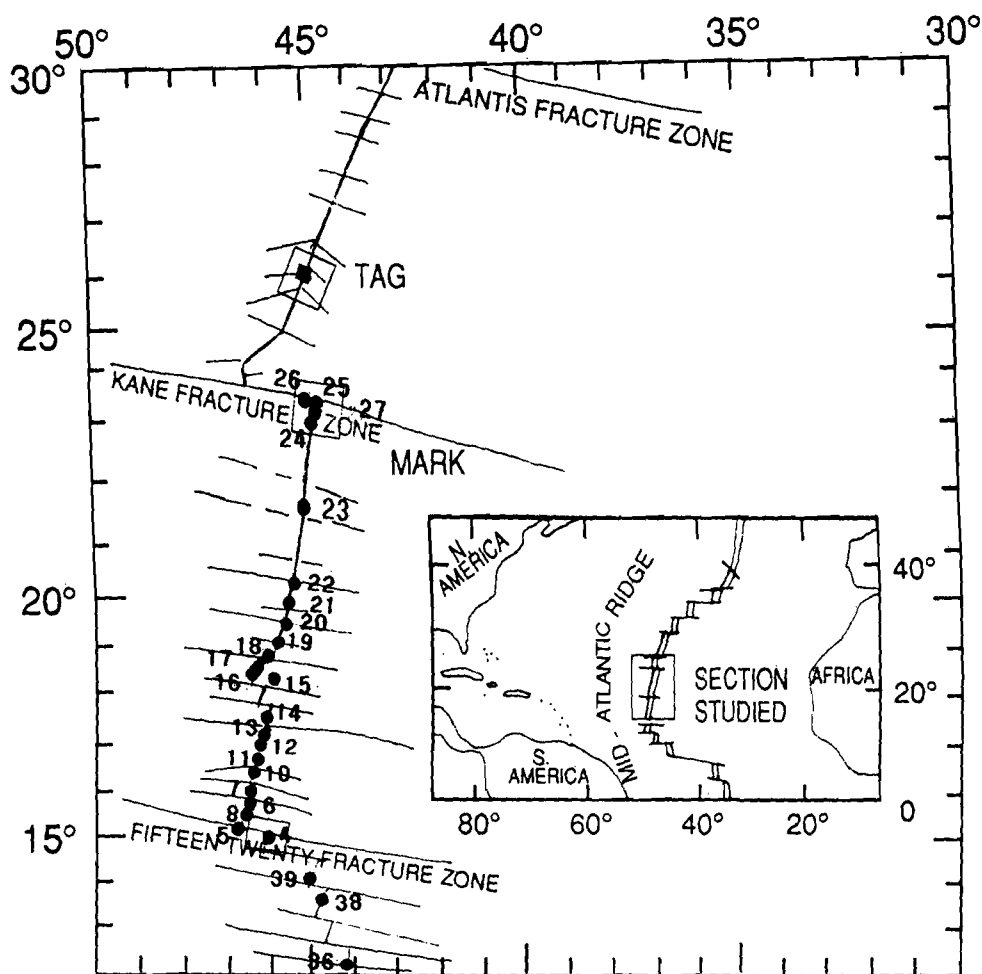


Fig. 1. Regional map of the Mid-Atlantic Ridge between 12°N and 26°N, showing locations of Fifteen Twenty Fracture Zone (FZ), MARK, and TAG areas. Solid circles mark the CTD vertical profiles conducted in the axial area during *Akademik Boris Petrov* (1985) (stations 36, 38, 39) and Ridelente (1988) (stations 4 to 27) cruises. Squares mark known venting sites TAG (26°N) and MARK (23°N) studied during *Atlantis III 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.*, 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 CH<sub>4</sub>-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.*, 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 [Plüger *et al.*, 1990]. CH<sub>4</sub> 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 CH<sub>4</sub> 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<sub>4</sub> 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 (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<sub>4</sub> Concentrations and Corresponding Water Depths

Station	Latitude N	Longitude W	Bottom Depth, m	Sample Depth, m	CH <sub>4</sub> maximum, nmol/kg	Gelological Feature
<i>Akademik Boris Petrov Cruise (1985)</i>						
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
<i>Ridelente Cruise (1988)</i>						
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
<i>MAR/88 Cruise (NOAA-MAR Program) (1988)</i>						
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

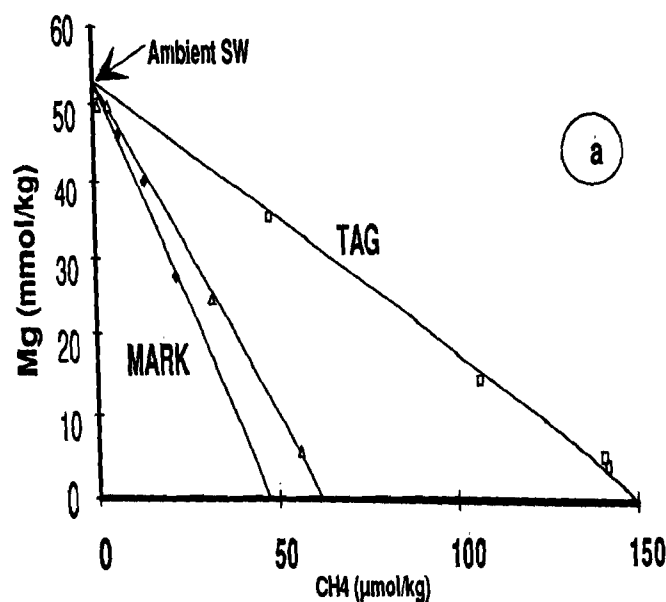
TFZ and UFZ are Marathon (12°N60'N) and Mercurius (12°20'N) Fracture Zones, respectively.

TABLE 2a. MAR/90 (*Atlantis II/Alvin* Cruise): CH<sub>4</sub> in the Neutrally Buoyant Plume Above TAG

Depth, m	Bottle	Si(OH) <sub>4</sub> , $\mu\text{mol/kg}$	Mn, nmol/kg	CH <sub>4</sub> , 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.

## TAG/MARK VENTS (1990)

TABLE 2b. MAR/90 (*Atlantis II/Alvin* Cruise): CH<sub>4</sub> in Buoyant Plumes Above TAG and MARK Sites

Dive	Bottle	Si(OH) <sub>4</sub> , $\mu\text{mol/kg}$	Mn, nmol/kg	Li, $\mu\text{mol/kg}$	CH <sub>4</sub> , 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.

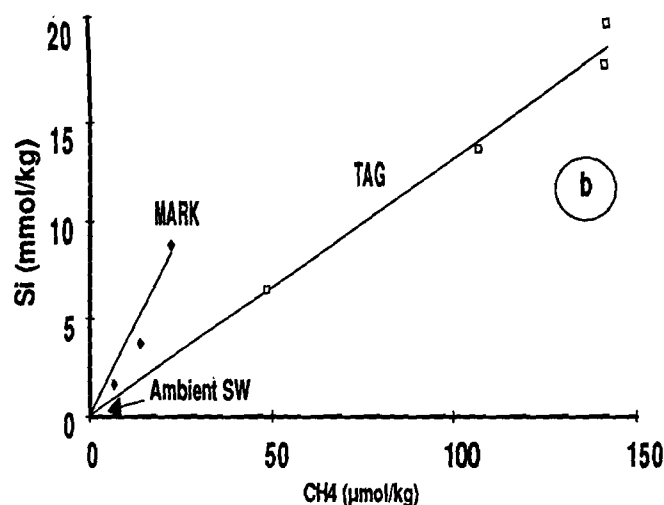


Fig. 2. MAR/90 (*Atlantis II/Alvin* cruise). (a) CH<sub>4</sub> end-members calculated for a zero Mg concentration in TAG (q) (150  $\mu\text{mol/kg}$ ) and MARK (n) (48  $\mu\text{mol/kg}$ ) fluids. CH<sub>4</sub> endmember (62  $\mu\text{mol/kg}$ ) obtained in fluids sampled during the French Hydrosnake (1988) cruise above MARK (D) are presented for comparison. (b) CH<sub>4</sub>/Si correlations found in the same TAG and MARK vent fluids.

TABLE 2c. MAR/90 (*Atlantis II/Alvin* Cruise): CH<sub>4</sub> in Hot Fluids From TAG and MARK Sites

Dive	Bottle	Temperature $^{\circ}\text{C}$	Mg, mmol/kg	pH	Si(OH) <sub>4</sub> , mmol/kg	H <sub>2</sub> S, mmol/kg	CH <sub>4</sub> *, $\mu\text{mol/kg}$	CH <sub>4</sub> **, $\mu\text{mol/kg}$
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  $\mu\text{mol/kg}$ ; Mn, 0.20 nmol/kg; Mg, 53 mmol/kg; CH<sub>4</sub>, 0.40 nmol/kg.

\* concentrations measured in samples,

\*\* End-members calculated by extrapolation for individual vents to zero magnesium. Chemical data, except CH<sub>4</sub>, are from A. Campbell (personal communication, 1990).

concentrations are similar to the extrapolated 1986 data [Edmond *et al.*, 1990]. A large  $\text{CH}_4$  content (endmember of  $150 \mu\text{mol/kg}$ ) was measured in the 1990 TAG vent samples (Table 2a).  $\text{CH}_4$  concentrations varying from 54 to  $670 \text{ nmol/kg}$  were found in the buoyant plume, while these values dropped to 0.9 to  $8.0 \text{ nmol/kg}$  in the neutrally buoyant part of the plume (Table 2b). A good correlation was observed in hot fluids between  $\text{CH}_4$  and silica with a  $\text{Si/CH}_4$  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 2b). This  $\text{CH}_4$  enrichment in fluids explains the  $\text{CH}_4$  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  $\text{CH}_4$  anomalies (up to  $9 \text{ nmol/kg}$ ) 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, $23^\circ \text{N}$ ) (Figure 3)

The MARK (or Snakepit) site at  $23^\circ 22.08' \text{N}$   $44^\circ 57.00' \text{W}$  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  $\text{CH}_4$  end-member calculated in high temperature ( $337^\circ\text{--}352^\circ\text{C}$ ) vent (Table 2c) samples showed values of 46 to  $49 \mu\text{mol/kg}$ . 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  $\text{CH}_4$  analysis on shore.  $\text{CH}_4$  and He gas concentrations are positively correlated with Mg contents. A mixing line calculation gives a  $\text{CH}_4$  end-member of  $62 \mu\text{mol/kg}$  (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  $\text{CH}_4$  was analyzed by the stripping/trapping method on shore.  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  decrease between 1988 and 1990 at the MARK site; however,  $\text{CH}_4$  concentration in the TAG fluids is surely 3 times higher than in the MARK fluids.  $\text{CH}_4$  concentrations found in Snakepit fluids are uniform and of the same order of magnitude as those found in the  $21^\circ \text{N}$  [Welhan and Craig, 1979, 1983] or  $13^\circ \text{N}$  [Merlivat *et al.*, 1987] fluids on the EPR.  $\text{CH}_4$  concentrations varying from 55 to  $326 \text{ nmol/kg}$  were observed in the buoyant plume immediately above the vents (Table 2b).

During the Ridelente cruise in 1988, four CTD/casts were conducted in the MARK area (Figure 4). A typical  $\text{CH}_4$  reference

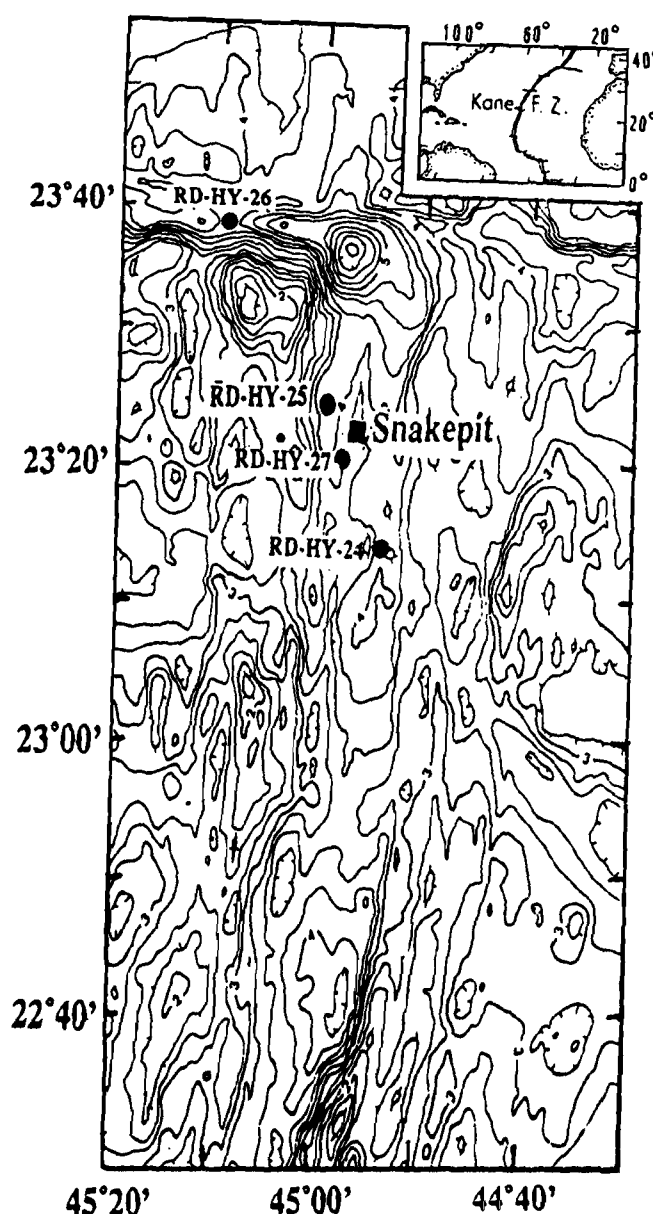


Fig. 3. Sea Beam map of the Snakepit hydrothermal area, south of the intersection of the MAR rift valley and the Kane FZ [Detrick *et al.*, 1984]. The square indicates the Snakepit hydrothermal field ( $23^\circ 22.08' \text{N}$   $44^\circ 57.00' \text{W}$ ). The Snakepit field is on the top of a large 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 ( $>40,000 \text{ m}^2$ ) 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  $23^\circ 39.55' \text{N}$  in the Kane FZ. RD-HY-25, just north of the MARK site, shows a  $\text{CH}_4$  plume ( $0.89 \text{ nmol/kg}$ ) 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  $\text{CH}_4$  anomalies of 1.34 and  $2.32 \text{ nmol/kg}$  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/ $15^\circ 20' \text{N}$ 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

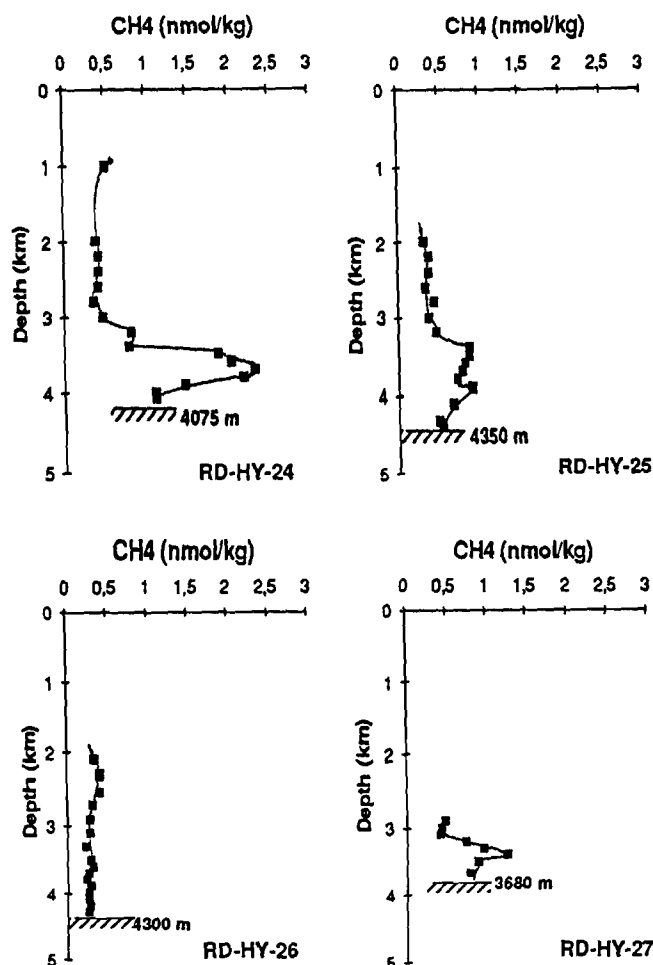


Fig. 4.  $\text{CH}_4$  concentration versus depth at stations RD-HY-24, 25, 26 and 27 conducted during the Ridelente cruise (1988), and around MARK area ( $23^\circ 22.08' \text{N}$ - $44^\circ 57.00' \text{W}$ ). RD-HY-26 conducted in Kane FZ, shows a  $\text{CH}_4$  profile near the background.

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  $15^\circ 20' \text{N}$  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/ $15^\circ 20' \text{N}$  FZ intersection was reported by Rona *et al.* [1987, 1988] and Bougault *et al.* [1990*ab*, this issue].

During the Ridelente cruise in 1988,  $\text{CH}_4$  anomalies reaching 2.7–3.6 nmol/kg were observed in the rift valley close to the eastern and western ridge axis/ $15^\circ 20' \text{N}$  FZ intersections [Charlou *et al.*, 1991c]. A  $\text{CH}_4$  profile (RD-HY-04) positioned at  $14^\circ 55.66' \text{N}$ - $44^\circ 55.20' \text{W}$  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],  $\text{CH}_4$  and Mn tracers were used to identify and compare hydrothermal plumes found above the TAG field ( $26^\circ \text{N}$ ) and in the rift valley at  $15^\circ \text{N}$  close to the eastern ridge axis/ $15^\circ 20' \text{N}$  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  $\text{CH}_4$  concentration (up to 8.9 nmol/kg) and elevated nephelometry signals. Plumes of a different composition were identified at  $15^\circ \text{N}$  with surprisingly high  $\text{CH}_4$  concentration (up to 17.6 nmol/kg),

associated with low total dissolved Mn concentration ( $\text{TDM} < 1$  nmol/kg) and no significant nephelometry signal [Charlou *et al.*, 1991c]. In the rift valley,  $\text{CH}_4$  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  $15^\circ 05' \text{N}$ - $44^\circ 59' \text{W}$ , from the eastern margin (water depth of 3400 m) to the dome top (water depth of 2500 m) exhibited an abrupt increase in  $\text{CH}_4$  (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  $\text{CH}_4$  (up to 6.7 nmol/kg) over the center. Relatively high  $\text{CH}_4$  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 ( $10 \mu\text{g/L}$ ) at the stations sampled in the rift valley and over the dome [Charlou *et al.*, 1991c; Rona *et al.*, 1992]. The  $15^\circ \text{N}$  plumes rising from the mount at 2500 and 2950 m exhibit large enrichment of  $\text{CH}_4$  with lesser TDM enrichment. The  $\text{CH}_4$  anomalies are clearly defined around 2500 and 3000 m depths, giving a typical bimodal shape for  $\text{CH}_4$  profiles in this area. This characteristic was never observed on  $\text{CH}_4$  profiles performed along the East Pacific Rise. It was found for the first time between  $12^\circ \text{N}$  and  $15^\circ \text{N}$  [Charlou *et al.*, 1988] on the MAR and remained unexplained at that time. Similar  $\text{CH}_4$  profiles were again found during the Ridelente cruise in 1988 between  $15^\circ \text{N}$  and  $23^\circ \text{N}$  at many places (Figure 7), indicating that they appear to be a common feature along the MAR.

#### Hydrothermal Activity in Other Areas Between $12^\circ$ and $23^\circ \text{N}$

Twenty CTD stations (Figure 7) were carried out between  $15^\circ \text{N}$  and  $23^\circ \text{N}$  during the Ridelente cruise in 1988. RD-HY-04 on the eastern ridge axis/ $15^\circ 20' \text{N}$  FZ intersection shows a  $\text{CH}_4$  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  $\text{CH}_4$  profiles were obtained on the western ridge axis/ $15^\circ 20' \text{N}$  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  $\text{CH}_4$  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 approximately 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  $16^\circ 37.42' \text{N}$  and  $16^\circ 91.68' \text{N}$ , respectively, show  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4 = 0.98$  nmol/kg) with characteristics similar to plumes observed at stations RD-HY-04, 05, 06. Between  $18^\circ \text{N}$  and  $20^\circ \text{N}$  (RD-HY-16, 17, 18, 19, 20),  $\text{CH}_4$  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  $\text{CH}_4$  profile near background, even though a slight anomaly can be detected at around 3000 m depth. Farther north,  $\text{CH}_4$  anomalies (0.89 nmol/kg) are again clearly defined on RD-HY-22 and 23 between

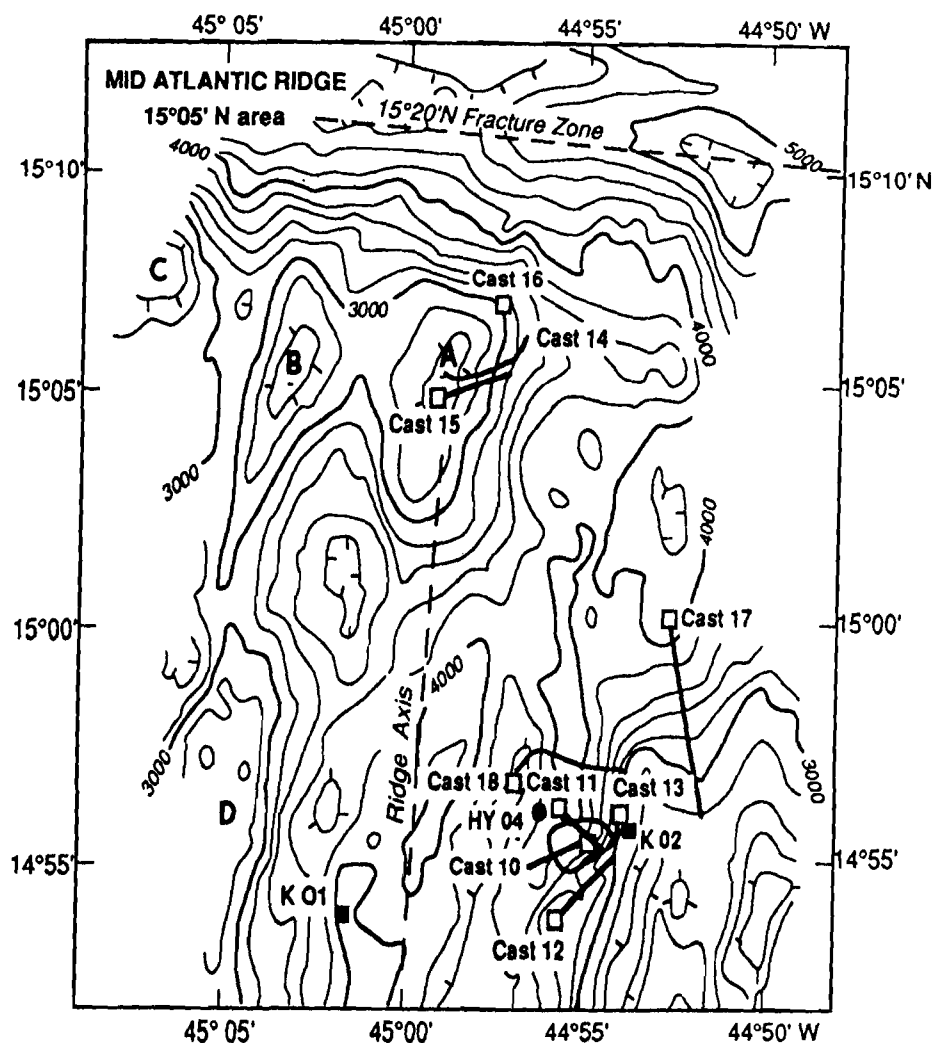


Fig. 5. Water column stations conducted on the east wall and axial dome close to the 15°20'N FZ./Ridge axis intersection during MAR/88 cruise (1988). The Sea Beam map was established during the Ridelente cruise (1988). The solid lines represent the CTD tracks and the open squares are the upcasts at the end of tows. K01 (14°53.8'N-45°01.6'W) and K02 (14°55.0'N-44°50.0'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  $\text{CH}_4$  profiles. Except for these two profiles, all other profiles show significant but variable  $\text{CH}_4$  anomalies along this MAR section. In addition, it can be observed that a  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  degassing is intense (Figure 9).

These results are compared to  $\text{CH}_4$  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  $\text{CH}_4$  anomaly at one station (HY-36), integrated over more than 1000 m, reflects a large  $\text{CH}_4$  input and then extensive hydrothermal activity on the inner floor and the valley walls. The occurrence of a small  $\text{CH}_4$  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 serpentinitization 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 (27-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

### $\text{CH}_4$ Plume Geometry on the MAR (Figure 8)

$\text{CH}_4$  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  $\text{CH}_4$  plumes rising up to 300 m above the seafloor in the rift valley. However, the various  $\text{CH}_4$  profiles observed along the MAR (Figure 8) show the thickness of the hydrothermally affected seawater column is up to 1 km, approximately 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].



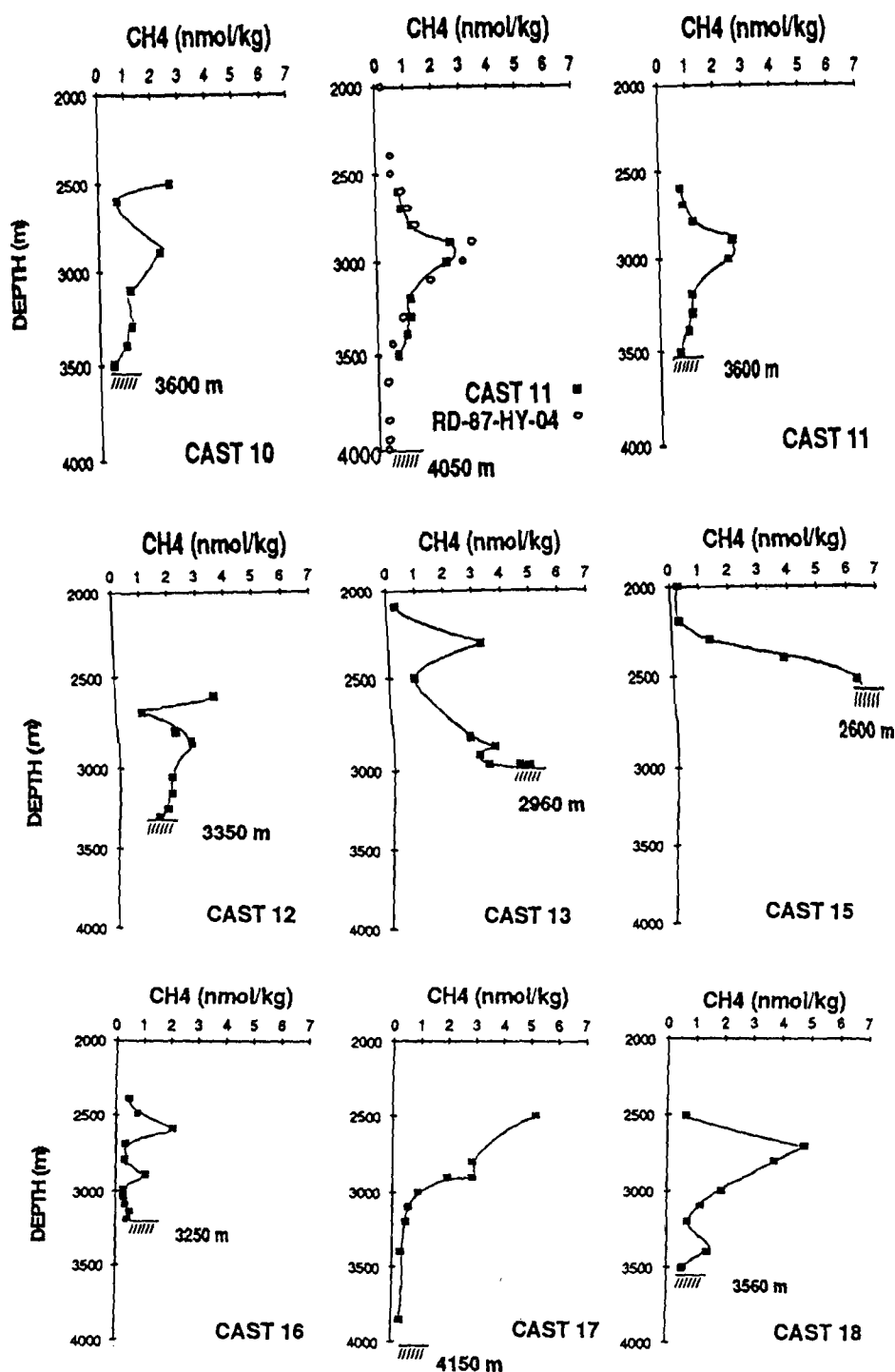


Fig. 6. Vertical profiles of  $\text{CH}_4$  for stations in the  $15^\circ\text{N}$  area. The  $\text{CH}_4$  profile (RD-HY-04) (open circles) obtained during the Ridelente cruise (1988) is superimposed on the  $\text{CH}_4$  profile of cast 11 (solid circles) obtained during MAR/88 cruise to show the good concordance between the 1985 and 1988 profiles.  $\text{CH}_4$  concentrations are elevated (up to  $6.7 \text{ nmol/kg}$ ) in cast 15 conducted just above dome A (Figure 5).  $\text{CH}_4$  plumes show maxima  $\text{CH}_4$  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  $\text{CH}_4$ , He or Mn plumes [Charlou *et al.*, 1991a]. Typical reference profiles found on the MAR and the EPR are presented respectively on Figures 8a and 8b. Figure 8c shows the  $\text{CH}_4$  profile observed at HF-19 station (Hydrofast cruise) [Charlou *et al.*, 1991a] near the  $13^\circ\text{N}$  hydrothermal site on the EPR. The  $\text{CH}_4$  plume is 300 m high and anomalies reach  $8 \text{ nmol/kg}$ . 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  $\text{CH}_4$  plume observed along the MAR between  $12^\circ$  and  $23^\circ\text{N}$  are shown in Figures 8e and 8f.

the topography of ridges. The vertical  $\text{CH}_4$  distribution between  $15^\circ\text{N}$  and  $23^\circ\text{N}$  along the MAR is distinct in both structure and intensity from that found along the EPR, such as at  $13^\circ\text{N}$  (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; Mott *et al.*, 1986].

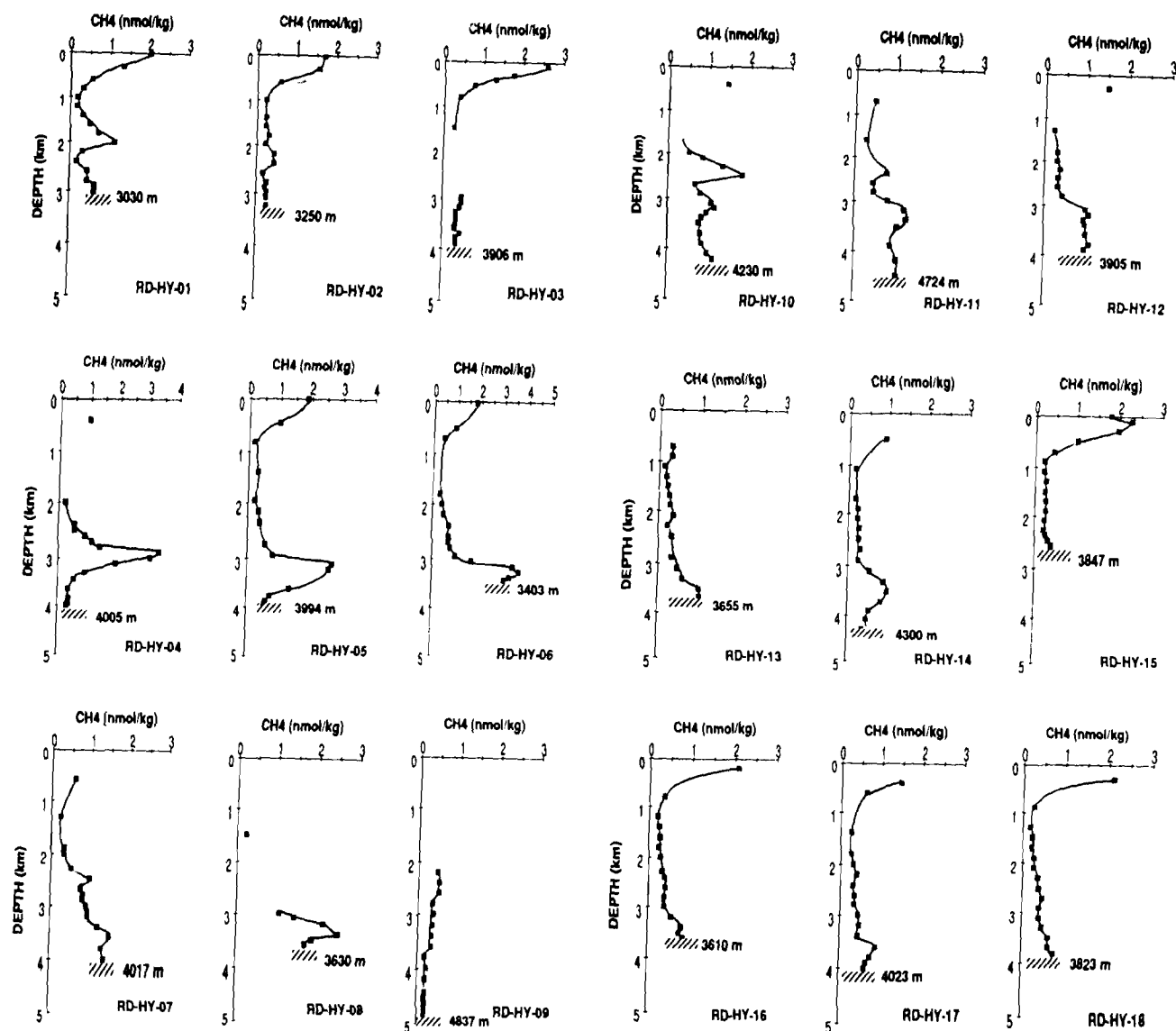


Fig. 7. CH<sub>4</sub> versus depth for stations sampled between 12° and 23°N during the Ridelente cruise (1988).

Fig. 7 (continued).

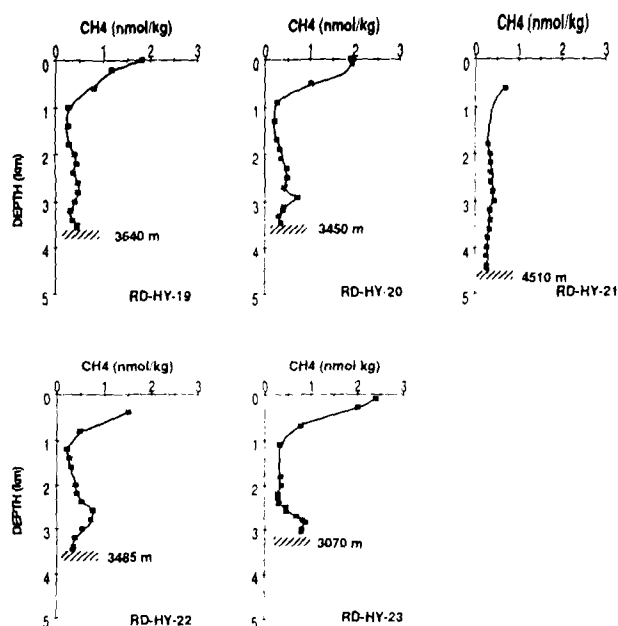


Fig. 7 (continued).

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<sub>4</sub> plumes emitted on the tops of the rift valley walls can be disseminated outside the rift valley (see RD-HY-10). The CH<sub>4</sub> 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). CH<sub>4</sub> 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<sub>4</sub> degassing decreases progressively from the inner floor to the top of the rift mountains. In addition, no CH<sub>4</sub> 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<sub>4</sub> degassing. On the EPR, the fluids extract light volatile elements such as H<sub>2</sub>, He, and CH<sub>4</sub> directly by leaching hot fresh basalt where these gases are present in great quantities. CO<sub>2</sub> and H<sub>2</sub>S in the 350°C fluids are in the range of 5–10 mmol/kg, while CH<sub>4</sub> and H<sub>2</sub> have been measured up to 0.1 and 2 mmol/kg [Kim *et al.*, 1984; Welhan and Craig, 1970, 1982; Medaris *et al.*, 1987]. Similar results were

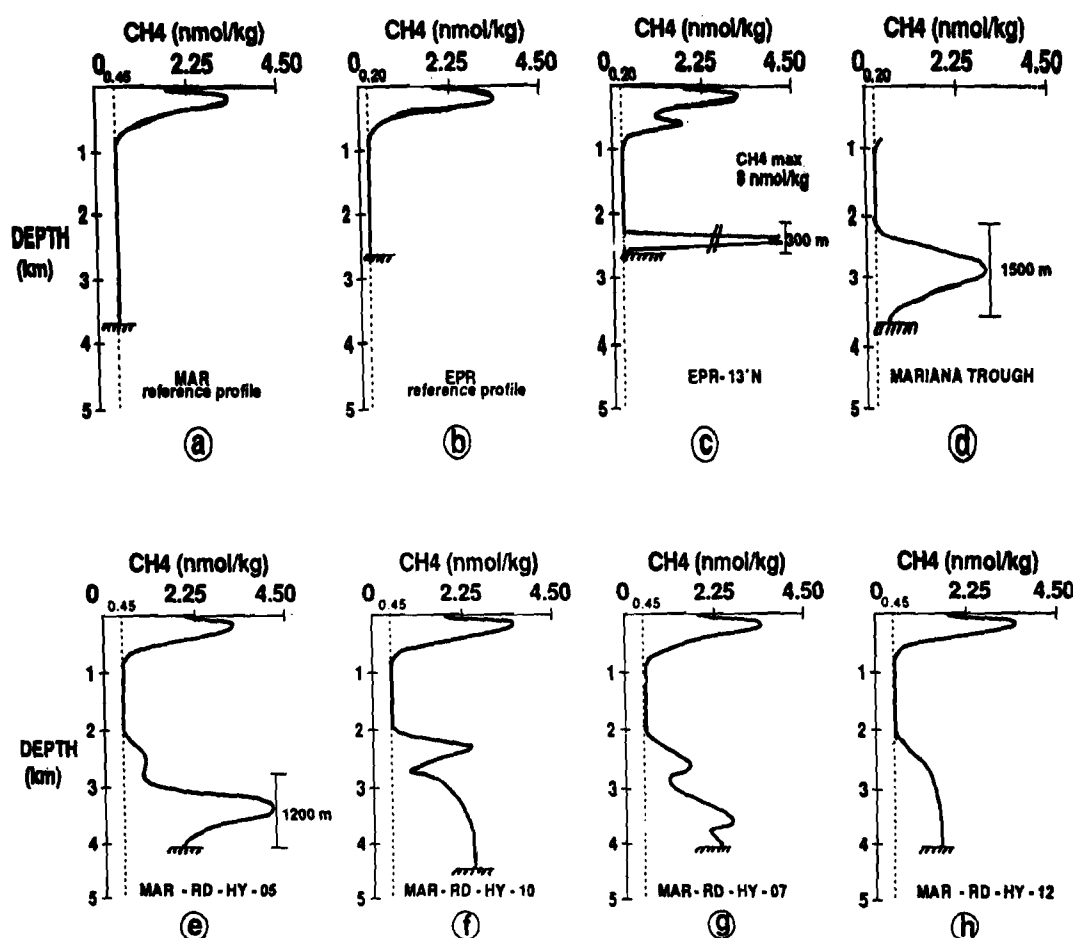


Fig. 8. CH<sub>4</sub> plume geometry observed along the Mid-Atlantic Ridge. (a) Typical CH<sub>4</sub> depth profile in the Atlantic Ocean without any detected anomaly. Station HY-14: 13°20.87'S-14°05.51'W; depth: 3570 m [after Charlou *et al.*, 1987]. (b) CH<sub>4</sub> depth profile at a control station in the Pacific Ocean [after Charlou *et al.*, 1991a]. (c) Hydrothermal CH<sub>4</sub> 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) CH<sub>4</sub> plume in the Mariana back arc spreading center [after Horibe *et al.*, 1986]. (e) MAR CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> plumes (stations RD-HY-07, 11 of the Ridelente cruise, (this work)). (h) CH<sub>4</sub> 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<sub>4</sub> has a clearly thermogenic origin as indicated by C<sub>1</sub>/(C<sub>2</sub>-C<sub>5</sub>) 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<sub>4</sub>/He ratio of 2.6 × 10<sup>6</sup> found in Snakepit fluids [Jean-Baptiste *et al.*, 1991] is similar to the CH<sub>4</sub>/He ratio found in MAR basalt glasses (0.7 × 10<sup>6</sup>) and in MAR volcanic "popping rocks" (2.1 × 10<sup>6</sup>) [Welhan and Craig, 1983; Pineau *et al.*, 1976], suggesting a nonbiogenic origin of CH<sub>4</sub> in this area. The CH<sub>4</sub> 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<sub>2</sub> and H<sub>2</sub>.

#### TDM and CH<sub>4</sub> in the Serpentinization Process: TDM/CH<sub>4</sub> Covariation

Some discrepancies have been shown to exist between total dissolvable manganese (TDM) and CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> concentrations and nephels and CH<sub>4</sub> 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<sub>4</sub>, 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<sub>4</sub>

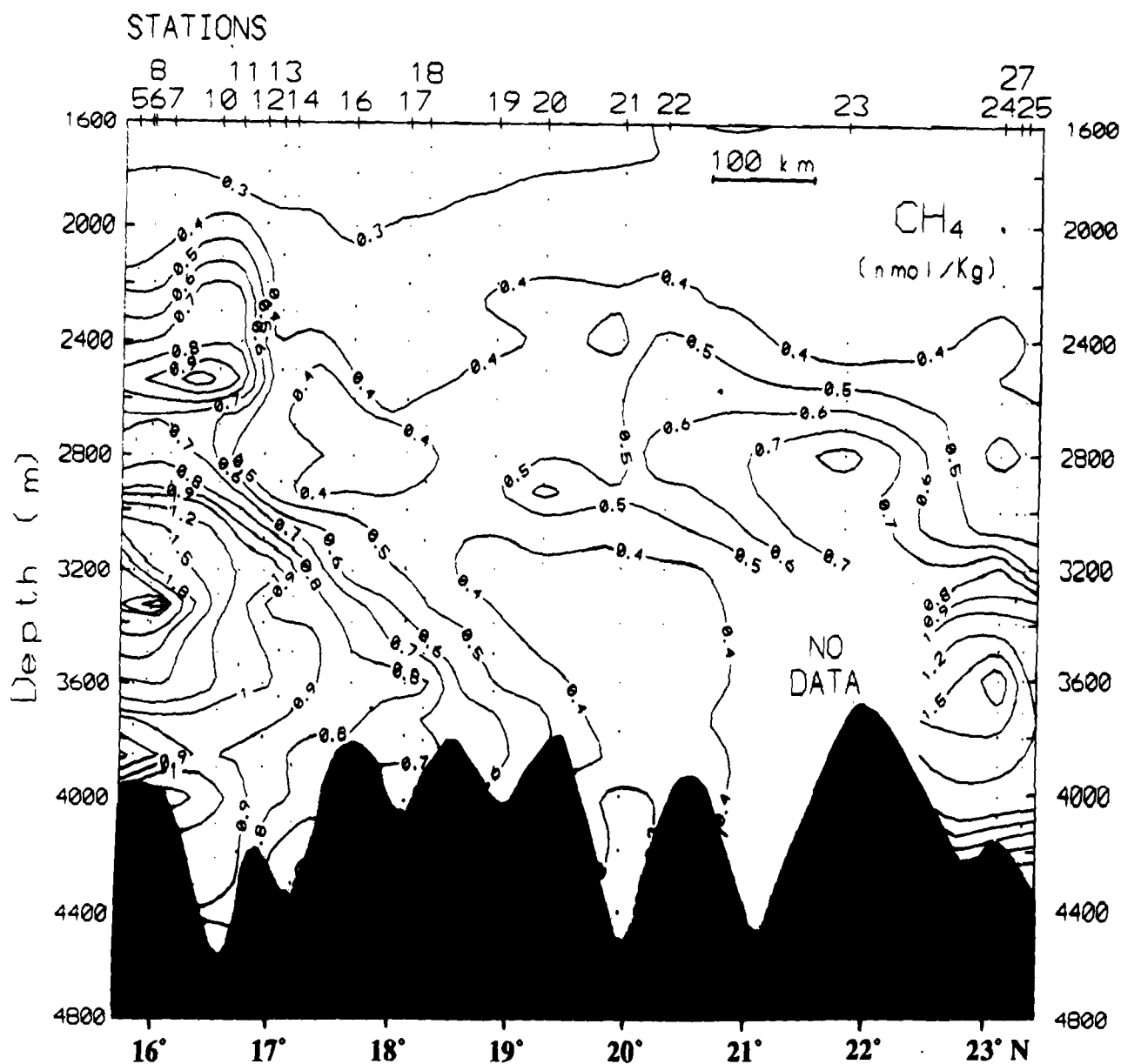


Fig. 9. Methane fields between 1600 m and the seafloor along the section 15°36'N / 23°N of the MAR. CH<sub>4</sub> plumes in the inner floor are clearly identified near the 15°20'N and Kane FZ. A CH<sub>4</sub> plume emitted at the top of rift mountains (2500 m) is defined around 16°30'N. Sample depths are indicated by dots (bottle data). The bathymetry of the ridge axis is schematic and very expanded.

TABLE 3. CH<sub>4</sub> End-members in Hydrothermal Fluids Compared to CH<sub>4</sub> Content in MORB Glasses

Location	CH <sub>4</sub> μmol/kg	References
<i>Hydrothermal Fluids</i>		
TAG (26°N) MAR	144	<i>This work</i>
Snakepit (23°N) MAR	62	<i>Jean-Baptiste et al. [1991]</i>
MARK Vent (23°N) MAR	45	<i>This work</i>
11°N EPR	67 - 117	<i>Kim et al. [1984]</i>
13°N EPR	27 - 54	<i>Merlivat et al. [1987]</i>
21°N EPR	58 - 90	<i>Welhan and Craig [1983]</i>
Galapagos	85 - 301	<i>Lilley et al. [1983]</i>
Guaymas Basin	12150 - 16650	<i>Welhan and Lupton [1987]</i>
southern, JDFR	81 - 117	<i>Evans et al. [1988]</i>
Axial Seamount, JDFR	25	<i>Butterfield et al. [1990]</i>
Endeavour, JDFR	504 - 1413	<i>Lilley et al. [1989]</i>
Lau Basin	3.6 - 4.5	<i>Charlou et al., [1992c]</i>
<i>MORB Glasses</i>		
MAR basalt glass	2.2 - 13.5	<i>Welhan and Craig [1983]</i>
EPR basalt Glass	0.6	<i>Welhan and Craig [1983]</i>
MAR popping rocks	12.6	<i>Welhan and Craig [1983]</i>

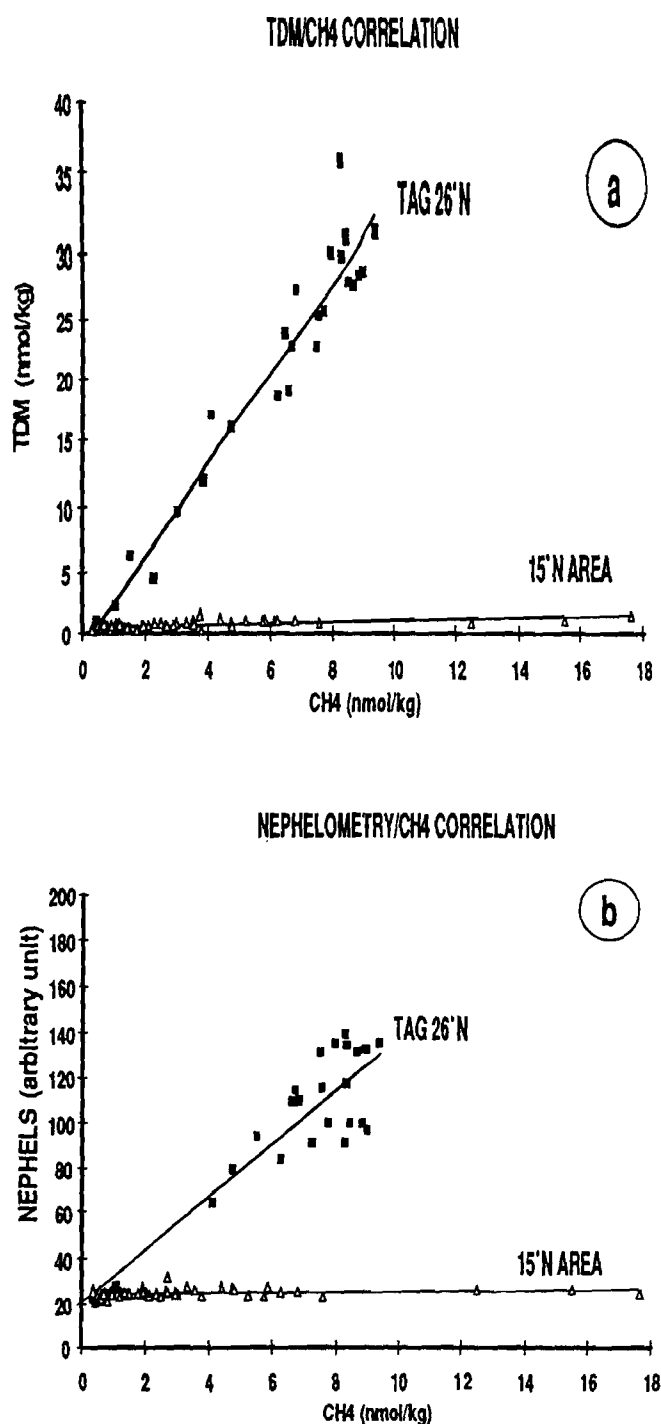


Fig. 10. Evidence of different hydrothermal processes from TDM/CH<sub>4</sub> and Nephel/CH<sub>4</sub> ratios at TAG (26°N) and 15°N area [Charlou *et al.*, 1991c; Rona *et al.*, 1992]. Nephels measurements are from T. Nelsen (NOAA-Miami) and TDM measurements are from P. Appriou (University of Brest, 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<sub>4</sub> concentration on the MAR (this work) is similar to that encountered elsewhere. The significant difference in TDM/CH<sub>4</sub> 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/CH<sub>4</sub> 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<sub>4</sub> 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 (pH=12.5) enriched in CH<sub>4</sub> 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 CH<sub>4</sub> (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 CH<sub>4</sub>, 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 CH<sub>4</sub> 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<sub>4</sub>. The ultramafic rock-seawater interaction as observed on the axial serpentinite dome (15°05'N) generates solutions with a high CH<sub>4</sub> content, probably associated with H<sub>2</sub> and CO<sub>2</sub> 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<sub>2</sub>-rich fluids at 300°C, 500 bars results in the generation of H<sub>2</sub> and in partial conversion of CO<sub>2</sub> to hydrocarbons [Janecky and Seyfried, 1986; Abrajano *et al.*, 1988; Szatmari, 1989]. In addition, H<sub>2</sub> 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<sub>2</sub>, formed by the reduction of H<sub>2</sub>O 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<sub>2</sub> enhances

hydrocarbon generation by hydrogenation. The reduction of  $\text{CO}_2$  through the Fischer-Tropsch synthesis produces  $\text{CH}_4$  and unsaturated hydrocarbons. In conclusion, conditions under which  $\text{CH}_4$  can be produced occur where there are adequate supplies of carbon and a suitable reductant (such as  $\text{H}_2$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^0$ ). These reduced gas occurrences are closely associated with mafic-ultramafic rocks. The presence of  $\text{H}_2$ - $\text{CH}_4$  gas seeps in serpentinized mafic-ultramafic rocks suggests a possible correlation between reduced gas formation and serpentinization. Magnetite, serpentine, brucite, and  $\text{H}_2$  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.  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ) trapped as fluid inclusions. The graphite crystals recovered in the vicinity of hydrothermal vents at  $13^\circ\text{N}$  on the EPR were formed during serpentinization by reaction of  $\text{CO}$  and/or  $\text{CO}_2$  [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 $12^\circ$ and $26^\circ\text{N}$ on the MAR

$\text{CH}_4$  profiles between  $12^\circ$  and  $26^\circ\text{N}$  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

$15^\circ\text{N}$  FZ/ridge axis intersections), where the permeability favors downwelling of seawater and serpentinization of ultramafic rocks (Figure 9). At  $15^\circ05'\text{N}$ , the  $\text{CH}_4$  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 ultrabasic bodies are uplifted as diapirs (clearly mapped at  $15^\circ05'\text{N}$ ) 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.  $\text{CH}_4$  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

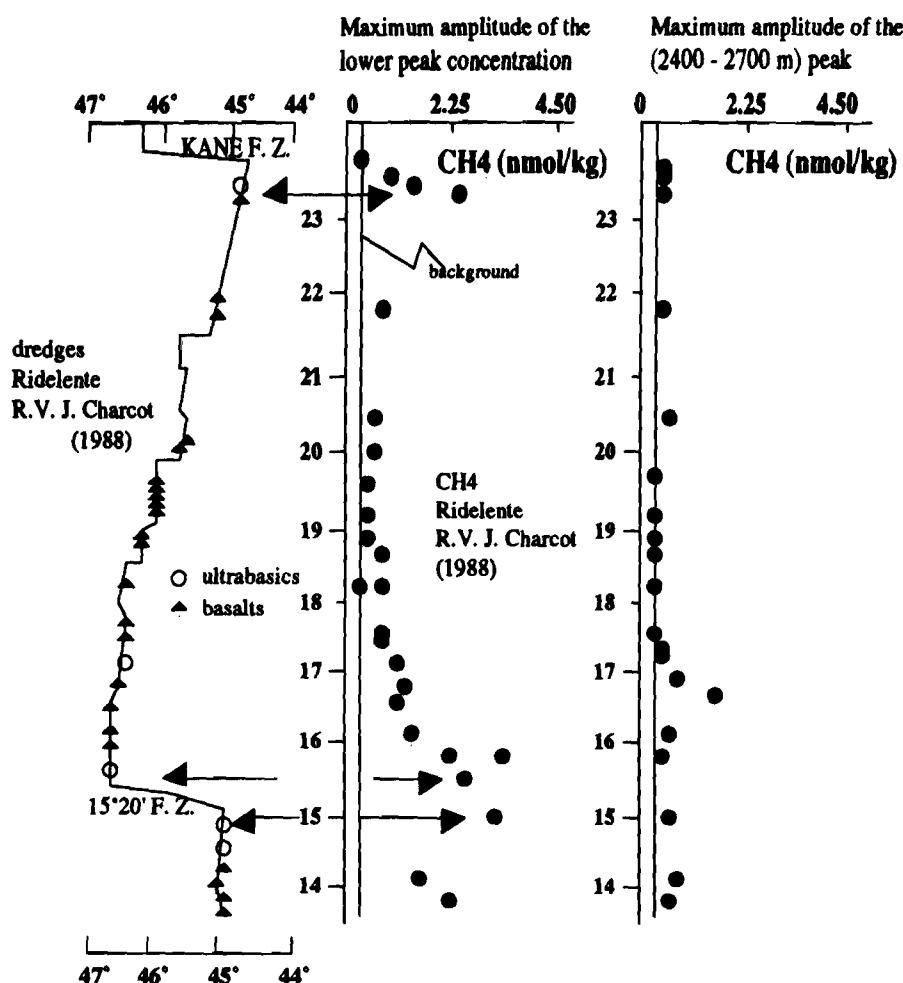


Fig. 11.  $\text{CH}_4$  variation between  $14^\circ\text{N}$  and  $23^\circ\text{N}$  along the MAR. The schematic ridge axis (after H.D. Needham, unpublished data, 1987) is represented on the left side. Solid triangles and open circles show respectively basalts and ultramafic rocks collected in dredges conducted in the CTD/cast areas. Solid circles represent maximum  $\text{CH}_4$  concentration measured on each profile in two seawater layers:  $\text{CH}_4$  maxima in the (2700-m bottom) layer (lower peak) in the middle, and  $\text{CH}_4$  maxima in the 2400-2700 m layer (upper peak) on the right side of the figure.  $\text{CH}_4$  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<sub>4</sub> is a good tracer of hydrothermal activity along mid-oceanic ridges. CH<sub>4</sub> 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<sub>4</sub> plumes. These CH<sub>4</sub> plumes have maxima above the two vent fields (TAG and MARK) known at the present time. The shape of CH<sub>4</sub> profiles clearly shows the water depth of sources, with CH<sub>4</sub> 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<sub>4</sub> and other chemical tracers (i.e., TDM/CH<sub>4</sub>) 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<sub>4</sub> and TDM data obtained along the MAR show that different TDM/CH<sub>4</sub> 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<sub>4</sub> ratio found above TAG and MARK areas is indicative of basalt-seawater interaction, while at 15°05'N the low TDM/CH<sub>4</sub> ratio provides evidence of fluid circulation in ultramafic rocks.

CH<sub>4</sub> 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 serpentinization of lower crustal and upper mantle ultramafic rocks. CH<sub>4</sub> investigations reveal and confirm the association between hydrothermal activity, serpentinization, diapirism and mantle degassing along the Mid-Atlantic Ridge.

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# REFERENCES

Abrajano, T. A., N. C. Sturchio, J. K. Bohlke, G. L. Lyon, R. J. Poreda, and C. M. Stevens, Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: Deep or shallow origin?, *Chem. Geol.*, 71,

- 211-222, 1988.
- Apps, J. A., Methane formation during hydrolysis by mafic rocks, Univ. of Calif., Lawrence Berkeley Lab., Berkeley, Calif., annual report, pp. 13-17, 1985.
- Auzende, J. M., J. P. Eissen, Y. Lafoy, P. Gente, and J. L. Charlou, Seafloor spreading in the North Fiji Basin (southwest Pacific), *Tectonophysics*, 146, 317-351, 1988.
- Baker, E. T., and G. J. Massoth, Characteristics of hydrothermal plumes from two vent fields on the Juan de Fuca Ridge, northeast Pacific Ocean, *Earth Planet. Sci. Lett.*, 85, 59-73, 1987.
- Baker, E. T., G. J. Massoth, R. W. Collier, J. H. Trefry, D. Kadko, T. A. Nelsen, P. A. Rona, and J. E. Lupton, Evidence for high-temperature hydrothermal venting on the Gorda Ridge northeast Pacific Ocean, *Deep-Sea Res.*, 34, 1461-1476, 1987a.
- Baker, E. T., G. J. Massoth, and R. A. Feely, Cataclysmic hydrothermal venting on the Juan de Fuca Ridge, *Nature*, 329, 149-151, 1987b.
- Baker, E. T., R. E. McDuff, and G. J. Massoth, Hydrothermal venting from the summit of a ridge axis seamount: Axial Volcano, Juan de Fuca Ridge, *J. Geophys. Res.*, 95, 12, 843-12,854, 1990.
- Baross, J. A., M. D. Lilley, and L. I. Gordon, Is the CH<sub>4</sub>, H<sub>2</sub> and CO venting from submarine hydrothermal systems produced by thermogenic bacteria?, *Nature*, 298, 366-368, 1982.
- Belviso, S., P. Jean-Baptiste, B. C. Nguyen, L. Merlivat, and L. Labeyrie, Deep methane maxima and He-3 anomalies across the Pacific entrance to the Celebes Basin, *Geochim. Cosmochim. Acta*, 51, 2673-2680, 1987.
- Blanc, G., J. Boulegue, and J. L. Charlou, Profils d'hydrocarbures légers dans l'eau de mer, les saumures et les eaux interstitielles de la fosse Atlantis II (Mer Rouge), *Oceanol. Acta*, 13, 187-197, 1990.
- Bougault, H., et al., Ridelente, Colloque Tour du Monde du Jean Charcot, 2-3 mars 1989, *Oceanol. Acta, sp. vol.*, 10, 366-381, 1990a.
- Bougault, H., J. L. Charlou, Y. Fouquet, and H. D. Needham, Activité hydrothermale et structure axiale des dorsales Est-Pacifique et médio-Atlantique, *Oceanol. Acta, sp. vol.*, 10, 199-207, 1990b.
- Bougault, H., J. L. Charlou, Y. Fouquet, H. D. Needham, N. Vaslet, P. Appriou, P. J. Baptiste, P. A. Rona, L. Dmitriev and S. Silantiev, Fast and slow spreading ridges: Structure and hydrothermal activity Ultramafic topographic highs, and CH<sub>4</sub> output, *J. Geophys. Res.*, this issue.
- Boulegue, J., and B. Hamelin, Activité hydrothermale de la dorsale Pacifique est à 21°30'S d'après des profils de concentration de manganèse dans l'eau de mer, *C. R. Acad. Sci.*, 297, 671-674, 1983.
- Butterfield, D. A., G. J. Massoth, R. E. Mac Duff, J. E. Lupton, and M. D. Lilley, Geochemistry of hydrothermal fluids from axial seamount hydrothermal emissions study vent field, Juan de Fuca Ridge: subseafloor boiling and subsequent fluid-rock interaction, *J. Geophys. Res.*, 95, 12895-12921, 1990.
- Campbell, A. C., T. S. Bowers, C.I. Measures, K. K. Falkner, M. Khadem, and J. M. Edmond, A time series of vent fluid compositions from 21°N, East Pacific Rise (1979, 1981, 1985), and the Guaymas Basin, Gulf of California (1982, 1985), *J. Geophys. Res.*, 93, 4537-4549, 1988a.
- Campbell, A. C., M. R. Palmer, G. P. Klinkhammer, T. S. Bowers, J. M. Edmond, J. R. Lawrence, J. F. Casey, G. Thompson, S. Humphris, P. Rona, and J. A. Karson, Chemistry of hot springs on the Mid-Atlantic Ridge, *Nature*, 335, 514-519, 1988b.
- Charlou, J. L., P. Rona, and H. Bougault, Methane anomalies over TAG hydrothermal field on Mid Atlantic Ridge, *J. Mar. Res.*, 45, 461-472, 1987.
- Charlou, J. L., L. Dmitriev, H. Bougault, and H. D. Needham, Hydrothermal CH<sub>4</sub> between 12°N and 15°N over the Mid-Atlantic Ridge, *Deep-Sea Res.*, 35, 121-131, 1988.
- Charlou, J. L., H. Bougault, P. Appriou, P. Jean-Baptiste, J. Etoubleau, and A. Birolleau, Water column anomalies associated with hydrothermal activity between 11°40' and 13°N on the East Pacific Rise: Discrepancies between tracers, *Deep Sea Res.*, 38, 569-596, 1991a.
- Charlou, J. L., J. P. Donval, Y. Fouquet, J. Erzinger, and U. von

- Stackelberg, Hydrothermal activity in the Lau Basin: Plumes and hot fluids chemistry, *Terra Abstr.*, 3, (1), 466, 1991b.
- Charlou, J. L., H. Bougault, P. Appriou, T. Nelsen, and P. Rona, Different TDM/CH<sub>4</sub> hydrothermal plume signatures: TAG site at 26°N and serpentinized ultrabasic diapir at 15°05'N on the Mid-Atlantic Ridge, *Geochim. Cosmochim. Acta*, 55, 3209-3222, 1991c.
- Coveney, R. M., E. D. Goebel, E. J. Zeller, G. A. M. Dreschoff, and E. E. Angino, Serpentinization and the origin of hydrogen gas in Kansas, *AAPG Bull.*, 71, 39-48, 1987.
- Cowen J. P., G. J. Massoth, and E. T. Baker, Bacterial scavenging of Mn and Fe in a mid to far field hydrothermal particle plume, *Nature*, 322, 169-171, 1986.
- Craig, H., W. B. Clarke, and M. A. Beg, Excess He-3 in deep water on the East Pacific Rise, *Earth Planet. Sci. Lett.*, 26, 125-132, 1975.
- Craig, H., Y. Horibe, and K. A. Farley, Hydrothermal vents in the Mariana Trough: Results of the first Alvin dives, *Eos Trans. AGU*, 68, 1531, 1987a.
- Craig, H., V. K. Craig, and K. R. Kim, Papatua expedition, I, Hydrothermal vent surveys in back arc basins: The Lau, N. Fiji, Woodlark and Manus basins and Havre Trough (abstract), *Eos Trans. AGU*, 68, 100, 1987b.
- de Angelis, M. A., Methane oxidation at deep sea hydrothermal vents and plumes, *Eos Trans. AGU*, 69, 1109, 1988.
- de Angelis, M. A., J. A. Baross, and M. D. Lilley, Elevated bacterial counts and CH<sub>4</sub> oxidation activity in deep-sea hydrothermal buoyant and lateral plumes, Endeavour Segment of the Juan de Fuca Ridge, *Eos Trans. AGU*, 71, 91, 1990.
- Detrick, R. S., P. J. Fox, K. Karstens, W. B. J. Ryan, L. Mayer, and J. Karson, A Seabeam survey of the Kane Fracture Zone and the adjacent Mid-Atlantic Ridge rift valley, *Eos Trans. AGU*, 65, 1106, 1984.
- Donval, J. P., D. Grimaud, M. Stievenard, H. Bougault, J. L. Charlou, P. Jean-Baptiste, A. Michard, and C. Mevel, Chemistry of hot springs on the Snakepit, Mid-Atlantic Ridge, *Terra Cognita*, 1, 325, 1989.
- Edmond, J. M., K. L. Von Damm, R. E. McDuff, and C. I. Measures, Chemistry of hot springs on the East Pacific Rise and their effluent dispersal, *Nature*, 297, 187-191, 1982.
- Edmond, J. M., A. C. Campbell, M. R. Palmer, and C. R. German, Geochemistry of hydrothermal fluids from the Mid-Atlantic Ridge: TAG & MARK 1990, *Eos Trans. AGU*, 71, 1650-1651, 1990.
- Emerson, S., S. Kalkorn, L. Jacobs, B. M. Tebo, K. H. Nealson and R. A. Rosson, Environmental oxidation rate of manganese, II, Bacterial catalysis, *Geochim. Cosmochim. Acta*, 46, 1073-1079, 1982.
- Evans, W. C., L. D. White, and J. B. Rapp, Geochemistry of some gases in hydrothermal fluids from the Southern Juan de Fuca Ridge, *J. Geophys. Res.*, 93, 15, 305-15,313, 1988.
- Fouquet, Y., et al., Hydrothermal activity in the Lau Basin-First results from the Nautilau cruise, *Eos Trans. AGU*, 71, 18, 678-679, 1990.
- Fouquet, Y., et al., Hydrothermal activity and metallogenesis in the Lau back-arc basin, *Nature*, 349, 778-781, 1991a.
- Fouquet, Y., et al., Hydrothermal activity in the Lau back-arc basin: Sulfides and water chemistry, *Geology*, 19, 303-306, 1991b.
- Gamo, T., J. L. Ishibashi, H. Sakai, and B. Tilbrook, Methane anomalies in seawater above the Loihi submarine summit area, Hawaii, *Geochim. Cosmochim. Acta*, 51, 2857-2864, 1987.
- German, C. R., G. Klinkhammer, J. M. Edmond, A. Mitra, and H. Elderfield, Hydrothermal scavenging of rare elements in the ocean, *Nature*, 345, 516-518, 1990.
- German, C. R., R. Mills, J. Blusztajn, A. P. Fleer, M. P. Nacon, N. C. Higgs, H. Elderfield, and J. Thomson, A geochemical study of metalliferous sediment from the TAG hydrothermal mound, 26°08'N, Mid-Atlantic Ridge, *J. Geophys. Res.*, this issue.
- Gold, T., and S. Soter, Abiogenic methane and the origin of petroleum, *Energy Explor. Exploit.*, 1, 89-104, 1982.
- Grimaud, D., J. I. Ishibashi, Y. Lagabriele, J. M. Auzende, and T. Urabe, Chemistry of hydrothermal fluids from the 17°S active site on the North-Fiji Basin Ridge (SW Pacific), *Chem. Geol.*, 93, 209-218, 1991.
- Haggerty, J. A., Evidence from fluid seeps atop serpentine seamounts in the Mariana Forearc: Clues for emplacement of the seamounts and their relationship to forearc tectonics, *Mar. Geol.*, 102, 293-309, 1991.
- Horibe, Y., K. R. Kim, and H. Craig, Off-ridge submarine hydrothermal vents: Back-arc spreading centers and hot spot seamounts, *Eos Trans. AGU*, 64, 724, 1983.
- Horibe, Y., K. R. Kim, and H. Craig, Hydrothermal methane plumes in the Mariana back-arc spreading centre, *Nature*, 324, 131-133, 1986.
- Janecky, D. R., and W. E. Seyfried, Hydrothermal serpentinization of peridotite within the oceanic crust: Experimental investigations of mineralogy and major element chemistry, *Geochim. Cosmochim. Acta*, 50, 1357-1378, 1986.
- Jean-Baptiste, P., S. Belviso, G. Alaux, B. C. Nguyen, and N. Mihapoulos, <sup>3</sup>He and methane in the Gulf of Aden, *Geochim. Cosmochim. Acta*, 54, 111-116, 1990.
- Jean-Baptiste, P., J. L. Charlou, M. Stievenard, J. P. Donval, H. Bougault, and C. Mevel, Helium and methane measurements in hydrothermal fluids from the Mid-Atlantic Ridge: The Snakepit site at 23°N, *Earth Planet. Sci. Lett.*, 106, 17-28, 1991.
- Jedwab, J., and J. Boulegue, Graphite crystals in hydrothermal vents, *Nature*, 310, 41-43, 1984.
- Jenkins, W. J., and W. B. Clarke, The distribution of He-3 in the western Atlantic Ocean, *Deep Sea Res.*, 23, 481-494, 1976.
- Jenkins, W. J., P. A. Rona, and J. M. Edmond, Excess <sup>3</sup>He in deep-water over the Mid-Atlantic Ridge at 26°N: Evidence of hydrothermal activity, *Earth Planet. Sci. Lett.*, 49, 39-44, 1980.
- Jones, C. J., and J. W. Murray, The geochemistry of manganese in the northeast Pacific Ocean off Washington, *Limnol. Oceanogr.*, 30, 81-92, 1985.
- Jones, C. J., H. P. Johnson and J. R. Delaney, Distribution of hydrothermal manganese over the Juan de Fuca Ridge, *Geophys. Res. Lett.*, 8, 873-876, 1981.
- Kadko, D. C., N. D. Rosenberg, J. E. Lupton, R. W. Collier, and M. D. Lilley, Chemical reaction rates and entrainment within the Endeavour Ridge hydrothermal plume, *Earth Planet. Sci. Lett.*, 99, 315-335, 1990.
- Karson, J. A., et al., Along axis variations in seafloor spreading in the MARK area, *Nature*, 328, 681-685, 1987.
- Kim, K. R., Methane and radioactive isotopes in submarine hydrothermal systems, Ph. D. thesis, Univ. of Calif., San Diego, 1983.
- Kim, K. R., J. A. Welhan, and H. Craig, The hydrothermal vent fields at 13°N and 11°N on the EPR: Alvin 1984 results (abstract), *Eos Trans. AGU*, 65, 973, 1984.
- Kimura, M., S. Uyeda, Y. Kato, T. Tanaka, M. Yamano, T. Gamo, H. Sakai, S. Kato, E. Izawa, and T. Oomori, Active hydrothermal mounds in the Okinawa Trough backarc basin, Japan, *Tectonophysics*, 145, 319-324, 1988.
- Klinkhammer, G., H. P. A. Rona, M. Greaves, and H. Elderfield, Hydrothermal manganese plumes in the Mid-Atlantic Ridge rift valley, *Nature*, 314, 727-731, 1985.
- Klinkhammer, G., H. Elderfield, M. Greaves, P. Rona, and T. Nelsen, Manganese geochemistry near high-temperature vents in the Mid-Atlantic Ridge rift valley, *Earth Planet. Sci. Lett.*, 80, 230-240, 1986.
- Lamontagne, J. W., J. W. Swinnerton, V. J. Linnenbom, and W. D. Smith, Methane concentrations in various marine environments, *J. Geophys. Res.*, 78, 5317-5324, 1973.
- Lamontagne, R. A., J. W. Swinnerton, and V. J. Linnenbom, C<sub>1</sub> - C<sub>4</sub> hydrocarbons in the North and South Pacific, *Tellus*, 26, 71-77, 1974.
- Lilley, J. A., M. A. De Angelis, and L. I. Gordon, CH<sub>4</sub>, H<sub>2</sub>, CO and N<sub>2</sub>O in submarine hydrothermal vent waters, *Nature*, 300, 48-50, 1982a.
- Lilley, M. D., J. A. Baross, and L. I. Gordon, Dissolved hydrogen and methane in Saanich Inlet, British Columbia, *Deep-Sea Res.*, 29, 1471-1484, 1982b.
- Lilley, M. D., J. A. Baross, and L. I. Gordon, Reduced gases and bacteria in hydrothermal fluids: The Galapagos spreading center and 21°N



- East Pacific Rise, in *Hydrothermal Processes at Seafloor Spreading Centers*, edited by P. A. Rona, K. Bostrom, L. Laubier, and K. L. Smith, Jr., pp. 411-419, Plenum, New York, 1983.
- Lilley, M. D., J. A. Baross, D. A. Butterfield, E. J. Olson, R. E. McDuff, S. A. Macko, J. A. Welhan, and C. N. Dahn, Volatile in Endeavour vent fluids, *Eos Trans AGU*, 70, 1163, 1989.
- Lupton, J. E., The  $^3\text{He}$  distribution in deep water over the Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.*, 32, 371-374, 1976.
- Lupton, J. E., Water hydrothermal plumes on the Juan de Fuca Ridge, *J. Geophys. Res.*, 95, 12,829-12,842, 1990.
- Lupton, J. E., and H. Craig, A major  $^3\text{He}$  source on the East Pacific Rise, *Science*, 214, 13-18, 1981.
- Lupton, J. E., J. R. Delaney, H. P. Johnson, and M. K. Tivey, Entrainment and vertical transport of deep-ocean water by buoyant hydrothermal plumes, *Nature*, 316, 621-623, 1985.
- Lupton, J. E., E. T. Baker, and G. J. Massoth, Variable  $^3\text{He}$ /heat ratios in submarine hydrothermal systems: evidence from two plumes over the Juan de Fuca Ridge, *Nature*, 337, 161-164, 1989.
- Merlivat, L., F. Pineau, and M. Javoy, Hydrothermal vent waters at  $13^\circ\text{N}$  on the East Pacific Rise: Isotopic composition and gas concentration, *Earth Planet. Sci. Lett.*, 84, 100-108, 1987.
- Michael, P. J., and E. Bonatti, Peridotite composition from the North Atlantic: Regional and tectonic variations and implications for partial melting, *Earth Planet. Sci. Lett.*, 73, 91-104, 1985.
- Michard, G., F. Albarede, A. Michard, J. F. Minster, J. L. Charlou, and N. Tan, Chemistry of solutions from the  $13^\circ\text{N}$  East Pacific Rise hydrothermal site, *Earth Planet. Sci. Lett.*, 67, 297-307, 1984.
- Mottl, M. J., and J. A. Haggerty, Upwelling of Cl-poor, S and C-rich waters through a serpentinite seamount, Mariana Forearc: ODP leg 125, *Eos Trans. AGU*, 70, 1382, 1989.
- Neal, C., and G. Stanger, Hydrogen generation from mantle source rocks in Oman, *Earth Planet. Sci. Lett.*, 66, 315-320, 1983.
- Nelsen, T. A., and E. B. Forde, The structure, mass and interactions of the hydrothermal plumes at  $26^\circ\text{N}$  on the Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.*, 106, 1-16, 1991.
- Nelsen, T. A., G. Klinkhammer, J. H. Trefry, and R. Trocine, Real-time observation of dispersed hydrothermal plumes using nephelometry: examples from the Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.*, 81, 245-252, 1986/87.
- Nelsen, T. A., J. H. Trefry, J. L. Charlou, P. Appriou, and P. A. Rona, Evidence of very large scale venting near the TAG hydrothermal field, *Eos Trans. AGU*, 44, 1271, 1988.
- Nojiri, Y., J. I. Ishibashi, T. Kawai, A. Otsuka, and H. Sakai, Hydrothermal plumes along the North Fiji Basin spreading axis, *Nature*, 342, 667-670, 1989.
- Pineau, F., M. Javoy, and Y. Bottinga,  $^{13}\text{C}/^{12}\text{C}$  ratios of rocks and inclusions in popping rocks of the Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.*, 29, 413-421, 1976.
- Pluger, W. L., et al., Discovery of hydrothermal fields at the central Indian Ridge, *Mar. Min.*, 9, 73-86, 1990.
- Rona, P. A., G. Thompson, M. Mottl, J. A. Karson, W. I. Jenkins, D. Graham, M. Mallette, K. Von Damm, and J. M. Edmond, Hydrothermal activity at the Trans-Atlantic Geotraverse hydrothermal field, Mid Atlantic Ridge crest at  $26^\circ\text{N}$ , *J. Geophys. Res.*, 89, 11,365-11,377, 1984.
- Rona, P. A., G. Klinkhammer, T. A. Nelsen, J. H. Trefry, and H. Elderfield, Black smokers, massive sulfides and vent biota at the Mid Atlantic Ridge, *Nature*, 321, 33-37, 1986.
- Rona, P. A., L. Widenfalk, and K. Bostrom, Serpentinized ultramafics and hydrothermal activity at the Mid-Atlantic Ridge crest near  $15^\circ\text{N}$ , *J. Geophys. Res.*, 92, 1417-1427, 1987.
- Rona, P. A., H. Bougault, J. L. Charlou, P. Appriou, T. A. Nelsen, J. H. Trefry, G. L. Eberhart, A. Barone, and H. D. Needham, Hydrothermal circulation, serpentinization, diapirism and degassing at a rift valley-fracture zone intersection, Mid-Atlantic Ridge near  $15^\circ\text{N}$ ,  $45^\circ\text{W}$ , *Eos Trans. AGU*, 69, 1271, 1988.
- Rona, P. A., H. Bougault, J. L. Charlou, P. Appriou, T. A. Nelsen, T. H. Trefry, G. L. Eberhart, A. Barone, and H. D. Needham, Hydrothermal circulation, serpentinization and degassing at a rift valley-fracture zone intersection: Mid-Atlantic Ridge near  $15^\circ\text{N}$ ,  $45^\circ\text{W}$ , *Geology*, 20, 783-786, 1992.
- Rosenberg, N. G., A new method for estimating the heat and chemical fluxes from a seafloor hydrothermal vent field, Ph. D. thesis, Univ. of Calif., Santa Barbara, 1988.
- Schoell, M., Multiple origins of methane in the Earth, *Chem. Geol.*, 71, 1-10, 1988.
- Scranton, M. I., and P. G. Brewer, Occurrence of methane in the near-surface waters of the western subtropical North Atlantic, *Deep Sea Res.*, 24, 127-138, 1977.
- Scranton, M. I., and P. G. Brewer, Consumption of dissolved methane in the deep ocean, *Limnol. Oceanogr.*, 23, 1207-1213, 1978.
- Sedwick, P. N., T. Gamo, and G. M. McMurtry, Manganese and methane anomalies in the North Fiji Basin, *Deep Sea Res.*, 37, 891-896, 1990.
- Simoneit, B. R. T., O. E. Kawka, and M. Brault, Origin of gases and condensates in the Guaymas Basin hydrothermal system (Gulf of California), *Chem. Geol.*, 71, 169-182, 1988.
- Speer, K. G., and P. A. Rona, A model of an Atlantic and Pacific hydrothermal plume, *J. Geophys. Res.*, 94, 6213-6220, 1989.
- Swinerton, J. W., and R. A. Lamontagne, Oceanic distribution of low-molecular-weight hydrocarbons-Baseline measurements, *Environ. Sci. Technol.*, 8, 657-663, 1974.
- Swinerton, J. W., and V. J. Linnenbom, Determination of  $\text{C}_1$  to  $\text{C}_4$  hydrocarbons in seawater by gas chromatography, *Anal. Chem.*, 34, 483-485, 1967.
- Szatmari, P., Petroleum formation by Fischer-Tropsch synthesis in plate tectonics, *A P G Bull.*, 73, 989-998, 1989.
- Thompson, G., S. E. Humphris, B. Schroeder, M. Sulanowska, and P. A. Rona, Active vents and massive sulfides at  $26^\circ\text{N}$  (TAG) and  $23^\circ\text{N}$  (Snakepit) on the Mid-Atlantic Ridge, *Can. Mineral.*, 26, 697-711, 1988.
- Trefry, J. H., R. P. Trocine, G. Klinkhammer, and P. A. Rona, Iron and copper enrichment of suspended particles in dispersed hydrothermal plumes along the Mid-Atlantic Ridge, *Geophys. Res. Lett.*, 12, 506-509, 1985.
- Trocine, R. P., and J. H. Trefry, Distribution and chemistry of suspended particles from an active hydrothermal vent site on the Mid-Atlantic Ridge at  $26^\circ\text{N}$ , *Earth Planet. Sci. Lett.*, 88, 1-15, 1988.
- Turner, J. S., and I. H. Campbell, Temperature, density and buoyancy fluxes in "black smoker" plumes, and the criterion for buoyancy reversal, *Earth Planet. Sci. Lett.*, 86, 85-92, 1987.
- Von Damm, K. L., and J. L. Bischoff, Chemistry of hydrothermal solutions from the southern Juan de Fuca Ridge, *J. Geophys. Res.*, 92, 11,334-11,346, 1987.
- Von Damm, K. L., J. M. Edmond, B. Grant, C. I. Measures, B. Wadden, and R. F. Weiss, Chemistry of submarine hydrothermal solutions at  $21^\circ\text{N}$ , East Pacific Rise, *Geochim. Cosmochim. Acta*, 49, 2197-2220, 1985a.
- Von Damm, K. L., J. M. Edmond, C. I. Measures, and B. Grant, Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California, *Geochim. Cosmochim. Acta*, 49, 2221-2237, 1985b.
- Ward, B. B., K. A. Kilpatrick, P. C. Novelli, and M. I. Scranton, Methane oxidation and methane fluxes in the Ocean surface layer and deep anoxic waters, *Nature*, 327, 226-229, 1987.
- Ward, B. B., K. A. Kilpatrick, A. E. Wopart, E. C. Minnich, and M. E. Lidstrom, Methane oxidation in Saanich Inlet during summer stratification, *Cont. Shelf Res.*, 9, 65-75, 1989.
- Welhan, J. A., Origins of methane in hydrothermal systems, *Chem. Geol.*, 71, 183-198, 1988.
- Welhan, J. A., and H. Craig, Methane and hydrogen in East Pacific Rise hydrothermal fluids, *Geophys. Res. Lett.*, 6, 829-831, 1979.
- Welhan, J. A., and H. Craig, Abiogenic methane in mid-ocean ridge hydrothermal fluids, in *Deep-Source-Gas Workshop Technical Proceedings*, edited by W. J. Gwilliam, Deep Source Gas Workshop Tech. Proc., Morgantown, W. Va, DOE-METC-82-50, pp. 122-128, 1982.

- Welhan, J. A., and H. Craig, Methane, hydrogen and helium in hydrothermal fluids at 21°N on the East Pacific Rise, in *Hydrothermal Processes at Seafloor Spreading Centers* edited by P. A. Rona, K. Bostrom, L. Laubier, and K. L. Smith, Jr., pp. 391-409, Plenum, New York, 1983.
- Welhan, J. A. and J. E. Lupton, Light hydrocarbon gases in Guaymas Basin hydrothermal fluids: Thermogenic v.s. abiogenic origin, *AAPG Bull.*, 71, 215-223, 1987.
- Whelan, J. K., B. R. T. Simoneit, and M. Tarafa, C<sub>1</sub>-C<sub>8</sub> hydrocarbons in sediments from Guaymas Basin, Gulf of California-Comparison to Peru Margin, Japan Trench and California Borderlands, *Org. Geochem.*, 12, 171-194, 1988.
- Winn, C. D., M. Karl, and G. J. Massoth, Microorganisms in deep-sea hydrothermal plumes, *Nature*, 320, 741-746, 1986.
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