PERGAMON

Deep-Sea Research II 45 (1998) 2665–2682

DEEP-SEA RESEARCH
PART II

Enriched H_2, CH_4, and ^3He concentrations in hydrothermal plumes associated with the 1996 Gorda Ridge eruptive event

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Received 15 January 1998; accepted 15 June 1998

Abstract

The rapid field response in March and April 1996 to diking-eruptive events on the Northern Gorda Ridge allowed the first detailed co-measurement of ^3He, H_2, and CH_4 in plumes associated with a submarine eruption, and examination of the chemical transformation of these volatile species during aging of the plumes. The diking-eruptive event generated extensive event plumes with a low ^3He/heat ratio of $\sim 0.4 \times 10^{-12}$ cm^3 STP gm^{-1} °C^{-1}, while chronic plumes had ^3He/heat ratios of $2.1–6.2 \times 10^{-12}$ cm^3 STP gm^{-1} °C^{-1}. Hydrogen concentrations in the initial event plume (EP96A) reached a maximum value of 47 nM, 235 times that of ocean background concentration (0.2 nM). In contrast, roughly one month later H_2 concentrations, although still elevated, had drastically dropped to 40 times background values. Methane concentrations in both event and chronic plume fluids were also elevated and similar to stable hydrothermal systems in unsedimented ridge environments, reaching a maximum value of 7 nM. The intense rapid interaction at very high temperatures of hydrothermal fluids with the host rock during dike intrusion or with seawater during extrusion of the basalt likely generated high, localized concentrations of H_2. The data indicate, however, that maximum rates of H_2 production during event plume formation could have lasted a few days at most. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The detection of event plumes in 1986 and 1987 on the Cleft Segment of the Juan de Fuca Ridge provided the initial evidence to suggest that submarine diking/eruptive

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PII: S0967-0645(98)00088-5

events are associated with the catastrophic and voluminous release of buoyant hydrothermal fluids that rise several hundreds of meters above the seafloor (Baker et al., 1987a, 1989, 1995a; Lupton et al., 1989; Lupton, 1995). In 1993, the discovery of a similar "megaplume" formed during an eruption on the CoAxial Segment of the Juan de Fuca Ridge (Baker et al., 1995b; Lupton et al., 1995; Embley et al., 1995) confirmed that these plumes are integral to submarine crustal accretionary processes (Delaney et al., 1994). Because the hydrothermal plumes integrate the heat and mass flux of fluids that saturate the porous sections of oceanic crust, they have the potential to be useful for studying a variety of hydrothermal and biological processes. Chemical species such as methane (CH_4), helium (^3He), manganese (Mn^{2+}), and hydrogen (H_2) are enriched within the plumes and all except ^3He are commonly used as chemical traces for shipboard detection of hydrothermal vents. The concentrations of these hydrothermal constituents and the ratios derived from them are valuable in evaluating plume dynamics and in gaining a first order understanding of the geochemistry of the underlying vent sites (Lupton et al., 1995; Lilley et al., 1995; Baker et al., 1995a). However, in past studies of event plumes triggered during submarine diking-eruptive events, real-time characterization of volatiles such as H_2 and CH_4 has not been possible because of the transient nature of the plumes and because of the extremely labile nature of many of the volatile species (de Angelis et al., 1993; Lilley et al., 1995; McLaughlin et al., 1996).

In mid-February 1996, intense seismicity was detected by the Navy's Sound Surveillance System (SOSUS) on the northernmost segment of the Gorda Ridge (Fox and Dziak, 1998). The character of the seismicity was believed to be indicative of a diking-eruptive event initiating near 42.75°N in the area of the Northern Gorda Ridge (Fox and Dziak, 1998). This detection resulted in one rapid response (GREAT 1; GR 1) and 2 follow-on field programs [GREAT 2 (GR 2) and GREAT 3 (GR 3)] in March, April, and June 1996, respectively (Cowen and Baker, 1998). During these field programs, the Northern Gorda Ridge was extensively studied by conductivity-temperature-depth-optical (CTDO) surveys and camera operations.

On March 10, a major event plume (EP96A) was detected rising nearly 1500 m above the seafloor with temperature and particulate anomalies found between 1800 and 2800 m, over a bottom depth of 3300 m (Baker, 1998). Subsequent vertical casts showed that the plume was roughly 1 km thick and extended 15 km along axis and at least 8 km across axis, with temperature anomalies ($\Delta\theta$) up to $\sim$0.12°C (Baker, 1998). In April 1996 a second distinct event plume (EP96B) was mapped to the south above the western valley wall between 1800 and 2400 m.

Camera surveys conducted during GR 2 confirmed the presence of a newly formed lava flow extending from 42.66°N to 42.69°N (Fig. 1; Chadwick et al., 1998). Using bathymetric anomalies determined from repeat swath mapping, Chadwick et al. (1998) calculate a minimum volume of this flow to be 0.02 km^3, roughly twice the volume of the CoAxial eruption (Chadwick et al., 1995). A second bathymetric anomaly to the south (Fig. 1) is thought to reflect a later eruption associated with seismic activity from March 10 to March 20, 1996 (Fox and Dziak, 1998). Event plume EP96B may have resulted from this volcanic event (Baker, 1998).

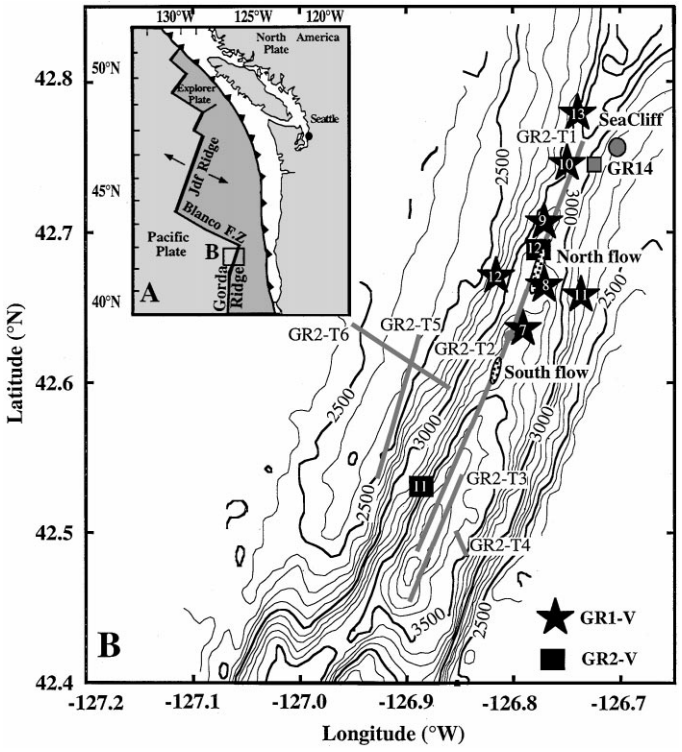

Fig. 1. (A) Location of Gorda Ridge. (B) Bathymetry of the Northern Gorda Ridge showing locations of a subset of CTDO tows and casts conducted during GR 1 and 2. The two small stippled areas denote the locations of topographic anomalies defined by Chadwick et al. (1998). The northernmost anomaly is the location of the lava flow imaged and mapped during GR 2, and the southern area is believed to be a subsequent eruptive flow. Vertical casts conducted during GR 1 are indicated by stars (GR1-V) and casts during GR 2 by squares (GR2-V). Track lines show the location of CTDO tows during GR 2. Also shown are the location of the Sea Cliff and GR 14 hydrothermal sites.

In this paper we report on volatile concentrations measured both in event plumes released during the 1996 Gorda diking-eruptive events and in associated chronic plumes. Although this is the third eruptive event in which both ^3He and heat have been measured, it is the first time in which H_2 values have been obtained. These volatile data are critical to evaluate the timing of plume formation and aging because H_2 is extremely labile in hydrothermal environments and its presence in high concentrations requires that the detected plume formed very recently and nearby (Lilley et al., 1995; McLaughlin, 1998). The rapid and significant decrease in concentration of volatiles such as H_2 in the plume fluids requires that very fast response times are needed to document the chemical character of plumes formed during diking-eruptive events.

2. Gorda Ridge setting

The 300 km long Gorda Ridge, located ~200 km west of the southern Oregon coast, is an intermediate rate spreading system (55 mm/yr—full rate) (Riddihough, 1980). The northern portion of the Gorda Ridge is characterized by a 3000–4000 m deep axial valley with a morphology more typical of a slow spreading rate environment. In contrast to the intermediate-spreading Juan de Fuca Ridge to the north, which exhibits a shallowly-rifted axial high morphology, the Northern Gorda Ridge is marked by a series of 400–600 m deep basins that extend along the axis of the rift valley. These basins shoal and narrow to a depth of ~2900 m near 42.73°N and 126.76°W. Active and inactive off-axis hydrothermal systems are located on the northeastern axial valley wall (SeaCliff and GR 14, Fig. 1). The GR 14 site extends for about 400 m along a northeast trend and vent temperatures of 100–247°C have been measured in this area (Rona and Clague, 1989; Rona et al., 1990). Camera surveys during GR 2 and a sidescan sonar survey completed during a subsequent cruise in August, 1996, show a well defined pillow ridge at the eruption site with extensive patches of bacterial mats (Chadwick et al., 1998; Johnson and Hutnak, 1997). A positive depth change anomaly indicates that the flow is up to 65 m in thickness with an estimated total volume of 16×10^6 m^3 (Chadwick et al., 1998). Temperature anomalies of 0.5°C were measured at 5–10 m off the bottom over the eruption site during the GR 2 camera tows (Chadwick et al., 1998). Thermal blanket measurements made on the summit of the flow 8 months after the eruption show that the flow was cooling rapidly with heat flux values of 4500 and 6950 mW/m^2 (Johnson and Hutnak, 1997).

3. Methods

Samples were collected from a 20 l bottle rosette package that included a high-precision Sea Bird 911 plus CTD and a Sea Tech light-scattering sensor (see Baker, 1998). Collection bottles were triggered during casts and CTDO tows and sampled for both background and plume water. Samples collected during GR 1 were drawn into 30 ml ground-glass stoppered bottles in a manner similar to the drawing of dissolved oxygen samples. Prior to sealing with a heavily greased stopper, 1 ml of saturated mercuric chloride solution was syringe-injected to inhibit biological activity. The samples were analyzed within a month on shore by gas chromatography in a manner similar to Lilley et al. (1996). For each analysis, aliquots were carefully drawn from the bottom of the sample bottles and treated as is described for shipboard analysis of GR 2 samples.

During GR 2, dissolved gases were determined by use of a single equilibration step between the water sample and a gas phase and subsequent analysis of the gas phase (McAullife, 1969). Specifically, 100 ml of bubble free fluid was drawn directly into 140 ml syringes followed by the addition of 40 ml headspace of ultra-high purity nitrogen. Insoluable H_2 and CH_4 were extracted into the headspace and hastened with vigorous shaking. The extraction efficiency (about 87% at these gas–water ratios) was checked by multiple equilibration steps with pure N_2. Extracted gases

were then analyzed with the highly sensitive Helium Ionization Detector (HID) (for H_2) and the Flame Ionization Detector (FID) (for CH_4). While sacrificing the high precision and accuracy of complete purge-and-trap injection techniques, this procedure allowed rapid analysis and detection of plume-borne reduced gases. A 5 ml aliquot of the headspace gas was injected onto a 6 m Hayessep A polymer column held at $-50°C$ and hydrogen was allowed to elute into the HID. The column was warmed to 100°C and the CH_4 backflushed to the FID. Detection limits for the two gases averaged about 0.04 ppm in the headspace gas, or about 0.5 nM (at room temperature and atmospheric pressure). Anatytical precision, determined by replicate injections of headspace gas was similarly about ± 0.04 ppm, however, sampling precision determined by analysis of replicate draws averaged ± 1 nM.

Upon recovery of the CTDO, samples for He analyses were immediately drawn and sealed into copper tubing using a special hydraulic crimping device (Young and Lupton, 1983). Helium concentrations and He isotope ratios were determined on a 21 cm radius, dual-collector mass spectrometer. Precision for the ^{3}He concentration measurements is 4×10^{-16} cc STP g^{-1}.

The hydrothermal temperature anomaly ($\Delta\theta$) values were obtained from Baker (1998) and reflect the excess heat in the plume fluids relative to background ocean water at a given depth and fluid density.

4. Results

4.1. GREAT 1

4.1.1. He/heat ratios

Measurements of ^{3}He and excess heat ($\Delta\theta$) in the GR 1 samples define two trends that exhibit dramatic variations in the ratio of $^3He/\Delta\theta$ (Fig. 2; Table 1). The event plume EP96A is best defined by stations GR1-V7-9, and GR1-V11 & V12, which exhibit a low $^3He/\Delta\theta$ ratio of 0.38×10^{-12} cm^3 STP g^{-1} °C^{-1} and the highest volatile enrichments (Figs. 1 and 2). The $^3He/\Delta\theta$ ratio of EP96A plume samples is similar to that of the Cleft and CoAxial event plumes, which had an average ratio of 0.3×10^{-12} cm^3 STP g^{-1} °C^{-1} (Table 1) (Lupton et al., 1989, 1995; Lupton, 1995). In contrast, samples from station GR1-V10, north of the eruption site, exhibit values more typical of deeper, steady-state plumes with a $^3He/\Delta\theta$ ratio of 3.2×10^{-12} cm^3 STP g^{-1} °C^{-1} (Figs. 1 and 2; Table 1). Station GR1-V10 is west of the GR 14 and SeaCliff hydrothermal sites. The higher $^3He/\Delta\theta$ ratio may reflect vent fluid input from within these two fields, which are located along the eastern axial valley wall at a depth of about 2700 m (Baker et al., 1987b; Rona and Clague, 1989; Rona et al., 1990).

4.1.2. ^{3}He, CH_4, and H_2 concentrations

The results of ^{3}He, CH_4, and H_2 gas measurements and station location for GR 1 are shown in Figs. 1–6. The sites nearest to the northern eruption, Stations GR1-V7, V8, and V9 exhibit the greatest water column enrichments of dissolved H_2 and ^{3}He (Figs. 3, 4 and 6), and lower $^3He/\Delta\theta$ ratios than those that characterize chronic

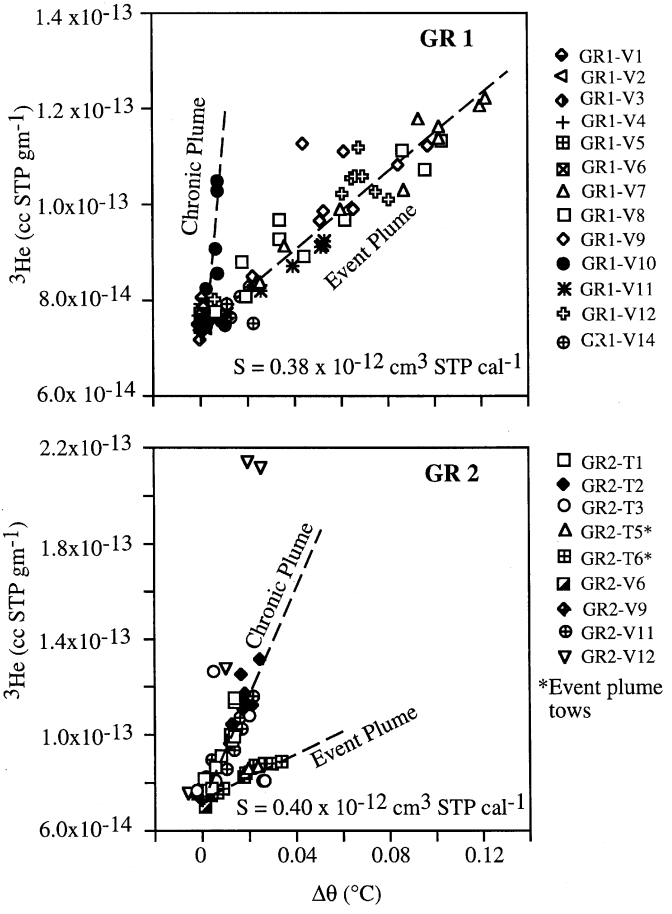

Fig. 2. Plot of ^{3}He and excess heat ($\Delta\theta$) for discrete samples taken during GR 1 and GR 2. EP96A and the subsequent event plume, EP96B are defined by ^{3}He/$\Delta\theta$ ratios (S) of 0.38 to 0.40×10^{-12} cm^3 STP g^{-1} °C^{-1}, which are typical of event plumes sampled to data. Samples from chronic plumes define a slope that varies from 1.9 to 3.2×10^{-12} cm^3 STP g^{-1} °C^{-1}. Samples from GR2-V12 (open triangles) that fall off of the slope that defines chronic plumes for EP96B, where taken directly above the northerly lava flow. These data indicate that the young flow had cooled rapidly, but that ^{3}He was still being degassed and entrained into the rising plume fluids (see text). Symbols denote samples taken during vertical casts (V) on GR 1 and GR 2, and tows (T) during GR 2.

plumes (Fig. 2). These data are consistent with volatile-heat derivation from a very recent magmatic eruptive event. Station GR1-V7, just south of the eruption site, exhibits the highest H_2 concentration with a value of 47 nM at a water depth of 2044 m (Figs. 3 and 4). This value is nearly 235 times that of ocean background water concentration (0.2 nM). Both ^{3}He and CH_4 show good correlation with H_2 at this depth with peak values of 12.2×10^{-14} cc STP g^{-1} and 6.5 nM (16 times background values), respectively. The volatile enrichment in the upper plume is also observed at

Table 1
Summary of Gorda Plume characteristics

Tow/Cast	$^3He/\Delta\theta$ (cm^3 STP/g°C)	$CH_4/^3He$	CH_4/Mn	$H_2/^3He$	H_2/Mn	References/comments
Great 1						Manganese values are from Massoth (1998)
EP96A GR1 V7–V9 (event)	$04.\times10^{-12}$	3.2×10^6	0.11	20.9×10^6	0.8	
GR1-V10 (chronic)	3.2×10^{-12}	1.0×10^6	0.5	3.4×10^6	—	
Great II						
GR2-V11	1.9×10^{-12}	1.0×10^6	0.05	1.6×10^6	0.06	
GR2-V12	6.2×10^{-12}	0.1×10^6	0.01	0.1×10^6	0.01	
EP96B (event)	0.4×10^{-12}	2.3×10^6	0.10	4.9×10^6	0.2	
N. Plume (chronic)	2.1×10^{-12}	0.7×10^6	0.05	$1.4\ (6.3)\times10^6$[a]	0.04 (0.25)	
S. Plume (chronic)	2.1×10^{-12}	1.7×10^6	0.05	$0.6\ (5.4)\times10^6$[a]	0.02 (0.10)	
1986 Cleft Event Plume	0.3×10^{-12}		0.3			Lupton et al. (1989), Massoth (pers. comm.)
1986 Cleft Chronic Plume	4.4×10^{-12}					Baker and Lupton (1990)
1993 CoAxial Event Plume	0.3×10^{-12}					Lupton et al. (1995)
1993 CoAxial Chronic Plume	1.9×10^{-12}					Lupton et al. (1995)
Theoretical upper mantle	2.0×10^{-12}					Lupton et al. (1989)

[a] Hydrogen in both plumes is heterogeneous, with isolated high H_2 values, reflected by the values in the parenthesis.

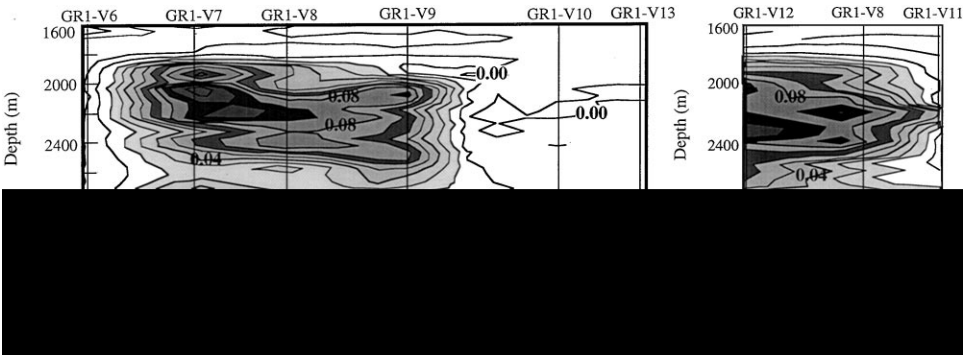

Fig. 3. Event plume EP96A as defined by along-axis (A) and cross-axis (B) temperature anomalies ($\Delta\theta$) mapped during GR 1 (after Baker, 1998). The plume was mapped by multiple vertical casts and is defined by the shaded areas (see Baker, 1998). Contour intervals are 0.01°C. Locations for each cast and two are shown in Fig. 1. The north lava flow associated with the formation of EP96A is marked by the black box (north flow). A topographic anomaly south of the north flow is believed to represent a subsequent eruptive event (* south flow) (Chadwick et al., 1998). Locations for vertical casts conducted during GR 1 are indicated by vertical lines (e.g. GR1-V7).

Station GR1-V8, which is the closest station to the eruption site (Figs. 3, 4, and 6), with ^{3}He and H_2 values of 11.3×10^{-14} cc STP g^{-1} and 35 nM, respectively, at a water depth of 1908 m. At Station GR1-V8, a second significant peak in ^{3}He occurred between ~2200 and 2400 m with values up to 12.2×10^{-14} cc STP g^{-1} and a corresponding H_2 concentration of 21 nM, indicating that the event plume was at least 560 m in vertical extent at this site. Elevated concentrations of ^{3}He (11.2×10^{-14} cc STP g^{-1}) and H_2 (17.7 nM) in the shallow plume also are found just a few hundred meters north of the eruption site at Station GR1-V9. However, ^{3}He and H_2 concentrations decrease dramatically at Station GR1-V10, ~5 km north of the flow (Figs. 3 and 4). This decrease in volatile concentrations to the north may reflect current forcing of the megaplume in a southerly direction. Results from vertical casts east and west of the eruption site (Stations GR1-V11 and GR1-V12), show that a moderate to intense ^{3}He anomaly is maintained across the basin axis with values of 9.2 and 11.2×10^{-14} cc STP g^{-1} at 2250 and 2100 m, respectively (Figs. 3 and 4). However, a corresponding enrichment in H_2 is not recorded at these water depths.

Below about 2400 m water depth, a strong correlation between H_2, ^{3}He, and CH_4 for GR 1 station is less well defined with variable enrichments in the three volatile species occurring at different depths and at different cast locations (Fig. 4). Station GR1-V7 and V8 show a second peak in ^{3}He concentration at 2800 m, while to the north at Stations GR1-V9 and V10 a peak in ^{3}He is recorded at ~2500 m. Associated moderate to slightly elevated concentrations in H_2 and CH_4 are observed in the plume at 2300–2700 m at Stations GR1-V7–9, and GR1-V12, with concentrations of H_2 and CH_4 up to 21 and 7 nM, respectively. Station GR1-V10 also shows a large inventory of deeper ^{3}He without an increase in either H_2 or CH_4.

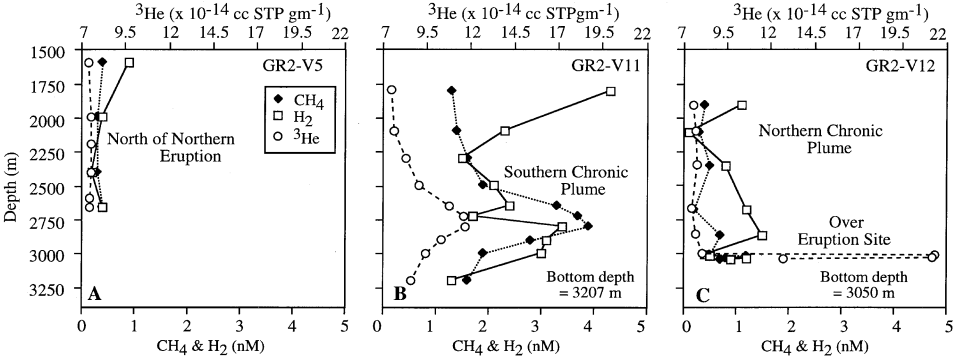

Fig. 8. Profiles of methane (CH_4), hydrogen (H_2) and helium (^3He) for discrete samples taken on vertical casts GR2-V5, -V11, and -V12 conducted during GR 2. The location of each profile with respect to the chronic plume locations is shown in Fig. 7. Volatile concentrations from samples north of the plume reflect input from chronic venting systems. The area of high volatile concentrations shown in Fig. 7B, corresponds to the core of the more intense southerly plume, which is believed to have originated from the southern eruption (Baker, 1998). The sharp increase in ^3He concentrations in deep fluids that are associated with a weak plume sampled during GR2-V12 (C) is located 10 m off the bottom and directly over the northern eruption. The high ^3He concentrations without a corresponding increase in H_2, likely indicate that although there was continued degassing of ^3He from the lava flow, the flow was cool enough that H_2 was no longer being produced by water–rock interactions.

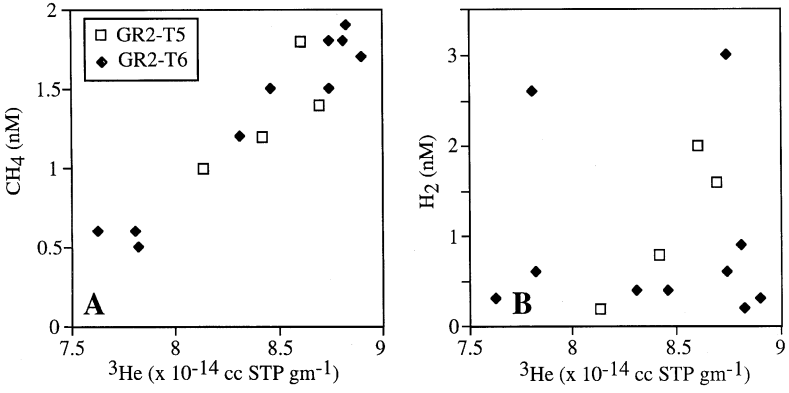

Fig. 9. Methane (CH_4) and helium (^3He) concentrations in the event plume EP96B measured on discrete samples from tows GR2-T5 and GR2-T6 during GR 2. Volatile concentrations are elevated above background values, but lower than those measured from EP96A.

lower steady-state plumes are 5–15 times higher than event plume fluids in the same localities (Table 1; Lupton et al., 1989, 1995). For example, stable venting systems that have been perturbed by magmatic events typically exhibit $^3He/\Delta\theta$ ratios of 1.9–4.4 cm^3 STP g^{-1} $°C^{-1}$ in contrast to event plumes which have $^3He/\Delta\theta$ ratios of 0.3–0.4 cm^3 STP g^{-1} $°C^{-1}$ (Table 1). Because ^3He and heat are conservative

hydrothermal tracers, corresponding measurements of $^3He/\Delta\theta$ and non-conservative tracers that exhibit varying residence times (e.g. H_2, CH_4, and Mn) allow assessment of the source fluids, chemical evolution of the event plume fluids, and possible effects of microbial activity on gas concentrations (Lupton, 1995; Lilley et al., 1995; Massoth et al., 1998).

The rapid initial response to the Gorda event and subsequent follow-up cruises permitted the sampling of volatile species in the plumes within days following the eruption(s), measurement of H_2 concentrations in event plume fluids in near real-time, and the tracking of heat and volatiles with aging of the plume fluids. Although co-measurement of ^3He, CH_4 and H_2 in discrete samples is particularly valuable in studies of plume formation, there are very few reports of H_2 concentrations associated with hydrothermal plumes in stable venting systems (Lilley et al., 1995) and the only other report of H_2 in plumes associated with submarine eruptive events is from Loihi Seamount (Sansone et al., 1996).

Recent experimental work has shown that a likely source of H_2 in hydrothermal systems is through high-temperature alteration of olivine (Berndt, 1996). This reaction was shown to occur very rapidly, implying that a "burst" of H_2 production may be associated with diking-eruptive events. This view is consistent with recent field observations. Large quantities of H_2 (up to 2 μM) were found in sea-surface plume fluids generated during direct interaction of Kilauea lava with seawater just subsequent to the flows entering the sea (Sansone et al., 1991). In submarine hydrothermal systems, H_2 increases have also been measured in vents perturbed by recent volcanic eruptions. Hydrogen in the "A" vent at 9°N had increased to at least 40 mM three weeks after the 1991 eruption and had declined to 1 mM eleven months later (Lilley et al., 1992). Plume fluids with H_2 concentrations of 20 nM were also measured following the Loihi eruptive event (Sansone et al., 1996).

The highly elevated and variable H_2 concentrations in EP96A, which correlate with well defined maxima in ^3He and temperature, show that plume formation had been on the order of days before its discovery; however, chemical aging of the plume had already begun (Fig. 5). During and shortly following the eruption of the two lava flows at Gorda, intense and rapid interaction of seawater with the flows likely generated high, localized concentrations of H_2 during very high-temperature seawater–rock interactions, both in the flow itself and in newly developed subseafloor fractures generated during the diking events. The low values of H_2 measured in the weakly developed plume associated with the northern eruption during GR 2 suggest that this flow cooled quickly and that the dominant period of H_2 generation was limited to the very early stages of the event. This interaction is consistent with thermal blanket results by Johnson and Hutnik (1997), which show that very early on in the history of the flows, heat flux was extremely high. The initial high permeability of the flow, coupled with intense convection of seawater leads to the prediction that the flow will cool within a few years after eruption (Johnson and Hutnik, 1997).

Methane concentrations in the Gorda plume fluids are similar to those from stable venting systems in unsedimented ridge environments, where concentrations typically range from 2 to 100 nM (Lilley et al., 1995). Seven months after the 9°N eruptive event CH_4 concentrations of up to 80 nM were measured in chronic plumes (Mottl

et al., 1995). Subsequent to the Loihi eruption, a value of 280 nM was measured for CH_4 in hydrothermal plumes that also had high particulate material (Sansone et al., 1996).

Methane in high-temperature hydrothermal environments can be generated by variety of mechanisms that include outgassing of juvenile CH_4, re-equilibration of CO_2 during cooling of the gases, thermal breakdown of complex hydrocarbons, and microbial production (Wehlan, 1988; Lilley et al., 1995; Kelley, 1996; Kelley and Früh-Green, 1995). Carbon stable isotope values are a common tool used to evaluate CH_4 sources, but we are hindered in hydrothermal work by a lack of knowledge of microbial fractionation factors at elevated temperatures (Lilley et al., 1983). The broad range of carbon isotopic values in high temperature hydrothermal systems ($\delta^{13}C = -9$ to $-50‰$ vs PDB; Kelley and Früh-Green, 1995; Lilley et al., 1993) indicates that complex source functions are acting in these environments. Hyperthermophilic methanogens have been isolated from diffuse vents at both 9°N on the East Pacific Rise and from the Endeavour Segment of the Juan de Fuca Ridge (M. Lilley, unpub. data), implying that microbial activity must be considered as a potential CH_4 source in diffuse flow environments.

The chemical transformation of volatile species in hydrothermal fluids during aging of the plumes is not well characterized. Initial measurements at the Endeavour Segment of the Juan de Fuca Ridge indicated that CH_4 had a residence time of approximately 10 days in the plume (Kadko et al., 1990). More comprehensive measurements of microbial CH_4 oxidation in plumes at Endeavour gave turn-over times ranging from one week to six months with the overall average being about two weeks (de Angelis et al., 1993). Measurements of microbial hydrogen oxidation made at Endeavour and at 9°N indicate turnover times ranging from about 7 h to a few days (Kadko et al., 1990; McLaughlin, 1998). Thus, the extremely elevated H_2 concentrations (47 nM) associated with the formation of EP96A requires that the plume was very young. Interestingly, the Station GR1-V7 values of greates H_2 and ^3He are the shallower samples and must indicate either a relatively "younger" age for these fluids than the waters immediately below, rapidly decreasing H_2 production rates, or large differences in microbial oxidation rates. This effect was not produced by variable dilution with seawater as ^3He does not decrease proportionally.

Ratios of CH_4/Mn and $CH_4/^3He$ in plumes have been used to infer the geochemical nature of the underlying hydrothermal system (Charlou et al., 1992; Ishibashi et al., 1995; Mottl et al., 1995, Lilley et al., 1995). These ratios for the various Gorda Ridge plumes, along with H_2/Mn and $H_2/^3He$, are shown in Table 1. As both CH_4 and H_2 are biologically labile, these ratios are a function of plume age and source composition and must be used with caution. The two event plumes (EP96A, EP96B) show elevated ratios of both H_2 and CH_4 to ^3He compared to the various chronic plumes, but the $H_2/^3He$ ratio is the more definitive in distinguishing between chronic and event plumes. This is consistent with recent findings that H_2 is produced in significant quantities during lava/seawater interactions (Sansone et al., 1996). In contrast, however, these field data indicate that CH_4 is not produced in significant quantities from transient high-temperature water/rock reactions associated with dike injection and eruption.

Based upon Fe and Mn data, Massoth et al. (1998), conclude that EP96B was roughly the same age when first sampled as EP96A. In contrast, our data (particularly $H_2/^3He$) do not show a significant H_2 enrichment in these fluids (Fig. 9), indicating either quite different source functions or that plume EP96B was older when sampled. The $CH_4/^3He$ ratio for EP96B is also consistent with this interpretation (Table 1).

There are presently two working hypotheses for the formation of event plumes. The first, based upon the low $^3He/\Delta\theta$ ratios in event plumes, assumes that the plume fluid is derived by the rapid expulsion of stored hydrothermal fluid from the upper crust by the magmatic event (Baker and Lupton, 1990; Lupton et al., 1995). The alternative (based upon fluid chemistry) is that interaction between ambient seawater and the lava flow or shallow dike produces event plumes (Butterfield et al., 1997). The data presented here do not definitely distinguish between these hypotheses. However, the localization of the highest H_2 concentrations in both time and space does provide some constraints. Hydrogen concentrations are distinctly higher in EP96A fluids sampled during GR 1 than those in the chronic plume from GR1-V10 and those in the two chronic plumes sampled during GR 2. Thus, consistent with the earlier discussion on H_2 production in hydrothermal systems, there is a definitive pulse of H_2 production associated with diking-eruptive events and it is most strongly displayed in the associated event plume. However, we are unable to defferentiate whether this pulse of H_2 production is produced by fresh rock interacting with stored hydrothermal fluid or with seawater. Although H_2 does not seem to be a useful indicator of the source fluids, the slightly elevated concentration of CH_4 in the event plume fluids, coupled with the field data from Kilauea (Sansone et al., 1991), which indicates that CH_4 is not produced during transient high-temperature alteration episodes associated with new eruptions, suggests that the source fluids for event plumes are from within the deeper crust and not from the lava flows.

Acknowledgements

This research was supported by the National Science Foundation (OCE 9612203) and the NOAA VENTS Program. Thanks to E.T. Baker for generously providing hydrographic data and for making figures available and to G.J. Massoth for providing Mn data. We thank R. Greene for collecting He samples at sea and L. Evans and R. Covar for laboratory analyses of the He samples. This manuscript benefited from the thoughtful comments of two anonymous reviewers.

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