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Hydrothermal fluid emanations from the submarine Kick'em Jenny volcano, Lesser Antilles island arc

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Abstract

Little is known about the role of island arcs as hydrothermal sources to the ocean when compared to the extensive research that has been carried out on hydrothermal systems at spreading ridges, although increasingly more work is being done on intraoceanic arcs. Here, we present fluid geochemistry data from the Kick'em Jenny (KeJ) submarine volcano of the Lesser Antilles island arc. Discharge of diffuse hydrothermal fluid was discovered on the southwestern flanks of the volcano. Hydrothermal input into the water column was recognized from CH_4 and trace-metal anomalies in water-column profiles in a depth range of 500–700 m. Samples collected directly on the seafloor also showed evidence for hydrothermal emissions where Mg and Cl were depleted in the fluids compared to ambient seawater, while CH_4 and several trace metals were enriched. The chemical composition of these samples, including O and H isotope data, suggests that the fluids are a mixture between a condensed vapor phase derived from a phase-separated hydrothermal fluid, which was conductively cooled in the sub-surface, and seawater. Increased dissolved organic carbon (DOC) concentrations of the fluids also indicate interaction with the sediment layer through which the fluids percolated. Although the volcanic crater could not be sampled directly due to safety concerns, δ^3He and some trace-metal values in seawater samples indicate fluid input containing a mantle component, probably from a hot, focused-flow source in the crater region around 200–300 m depth.

Keywords: Lesser Antilles; island arc; Kick'em Jenny volcano; submarine hydrothermal venting; fluid geochemistry

1. Introduction

Hydrothermal activity at mid-ocean ridges (MOR) has been the focus of many geochemical investigations since the discovery of seafloor hydrothermal systems in 1977 (e.g., von Damm, 1995). These hydrothermal fluxes play a significant role in the oceanic budgets for many dissolved metals (e.g. Sr, Fe, Mn). By contrast, much less is known about the role of seafloor hydrothermal activity along submarine volcanic arcs in terms of the element budgets of the ocean. A number of studies report on the compositions of arc-related hydrothermal mineral deposits (e.g., Glasby et al., 2000; Glasby and Notsu, 2003; Petersen et al., 2002),

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but little has been published about the chemistry of fluids. Available data are mostly from Pacific sites (e.g., de Ronde et al., 2001; 2003a,b; 2005; Gamo et al., 1997; Ishibashi and Urabe, 1995) and suggest that vent fluids produced by submarine volcanism and hydrothermal activity in intraoceanic arcs and back-arc systems differ in composition from those originating at MORs, and may represent an important source of gases and trace metals to the ocean. Eruptive activity together with hydrothermal discharge has also recently been described for a submarine arc volcano along the Mariana intraoceanic arc (Embley et al., 2006). Moreover, with exception of some plume survey work done along the Lihir island arc offshore Papua New Guinea (de Ronde et al., 2003a,b) and for Kavachi volcano of the Solomons island arc (Baker et al., 2002) little work has been done on submarine volcanoes and vents of the submerged portions of island arcs.

The focus of this study was to determine the composition of hydrothermal fluids from the Kick'em Jenny (KeJ) submarine volcano, which is located at the southern part of the Lesser Antilles (Fig. 1a). Widespread submarine volcanic activity along the Lesser Antilles island arc is well documented (e.g., Polyak et al., 1992; Devine and Sigurdsson, 1995). However, little information is available about submarine venting of hydrothermal fluids along this arc. Shallow-water hot springs are known along the coasts of some of the islands, such as Dominica, St. Lucia and Montserrat (Johnson and Cronan, 2001), although very little information is available for deeper waters (i.e. Polyak et al., 1992).

In an attempt to provide more information on submarine hydrothermal venting along the Lesser Antilles island arc, a research cruise with the German vessel *R/V Sonne* (SO 154, CARIBFLUX) was carried out in January/February 2001, covering four separate locations between Montserrat and Grenada (Halbach et al., 2002; Fig. 1a). Although no focused-flow hydrothermal vents were directly sampled during the expedition, evidence for hydrothermal components in the water column was detected and hydrothermal precipitates (e.g., ferromanganese crusts) collected (Frank et al., 2006). In the areas offshore Montserrat, Dominica and St. Lucia, only limited evidence for hydrothermal activity was noted in the water column, including slight increases in CH_4 concentrations and reduced Cr(III) species (Sander et al., 2003). The best evidence for hydrothermal emissions was noted close to the KeJ submarine volcano, northwest of Grenada. This volcano is located on the western slope of the Lesser Antilles island arc, where oceanic crust is subducted westward under the Caribbean plate. Hydrothermal activity has been observed on the crater floor of KeJ (Devine and Sigurdsson, 1995; Wishner et al., 2005). Bacterial mats and focused venting, (up to 70 °C), commonly accompanied by gas bubbles, occur at a depth of 250 m at the summit, although were not observed on the flanks of the volcano. No chemical data is available from these earlier investigations.

The summit crater of KeJ could not be mapped and sampled during the CARIBFLUX cruise due to safety concerns, as a result of increased seismic activity associated with the volcano. However, we detected significant input of hydrothermal fluids into the water column over the flanks of the volcano and also found indications of hydrothermal fluid venting from the crater region. Here, we present for the first time geochemical data on the hydrothermal fluids emanating from KeJ volcano. The unusual composition of the hydrothermal fluids together with evidence for a significant hydrothermal signal in the water column around KeJ volcano support the view that hydrothermal activity associated with submarine volcanic arcs – including both the submarine portion of island arcs and the more commonly studied intraoceanic arcs – may play an important role in the fluxes of various elements to the ocean, with notable differences in the chemistry of the venting along these arcs when compared to MOR systems (see e.g., von Damm, 1995).

2. Geologic setting and sampling sites

The basement to the Lesser Antilles consists of Eocene MOR-type basalts and sedimentary rocks of several km thickness (Eocene and Oligocene volcaniclastics), which were formed during Tertiary age spreading of the Grenada basin. These rocks are overlain by volcanic rocks of the modern island arc (Speed et al., 1997). Outcrops of sedimentary rocks occur at the northern coast and shelf of Grenada, and along the western shelf slope.

The location of KeJ north of Grenada (Fig. 1a) is possibly controlled by faults (Sigurdsson and Sheperd, 1974). The steep western flank of the island arc is characterized by N–S-trending, deeply penetrating normal faults caused by the uplift of the Lesser Antilles Platform, relative to the Grenada Basin in late Miocene (with initial volcanism due to the onset of subduction).

Observations made of the ocean floor during SO 154 by camera tows showed several faults with offsets up to 10 m along the southern flank of KeJ. These faults are either related to local stresses during volcano formation, or have been formed due to oblique subduction of the oceanic crust. Outcrops of basaltic dikes and massive rocks were also observed.

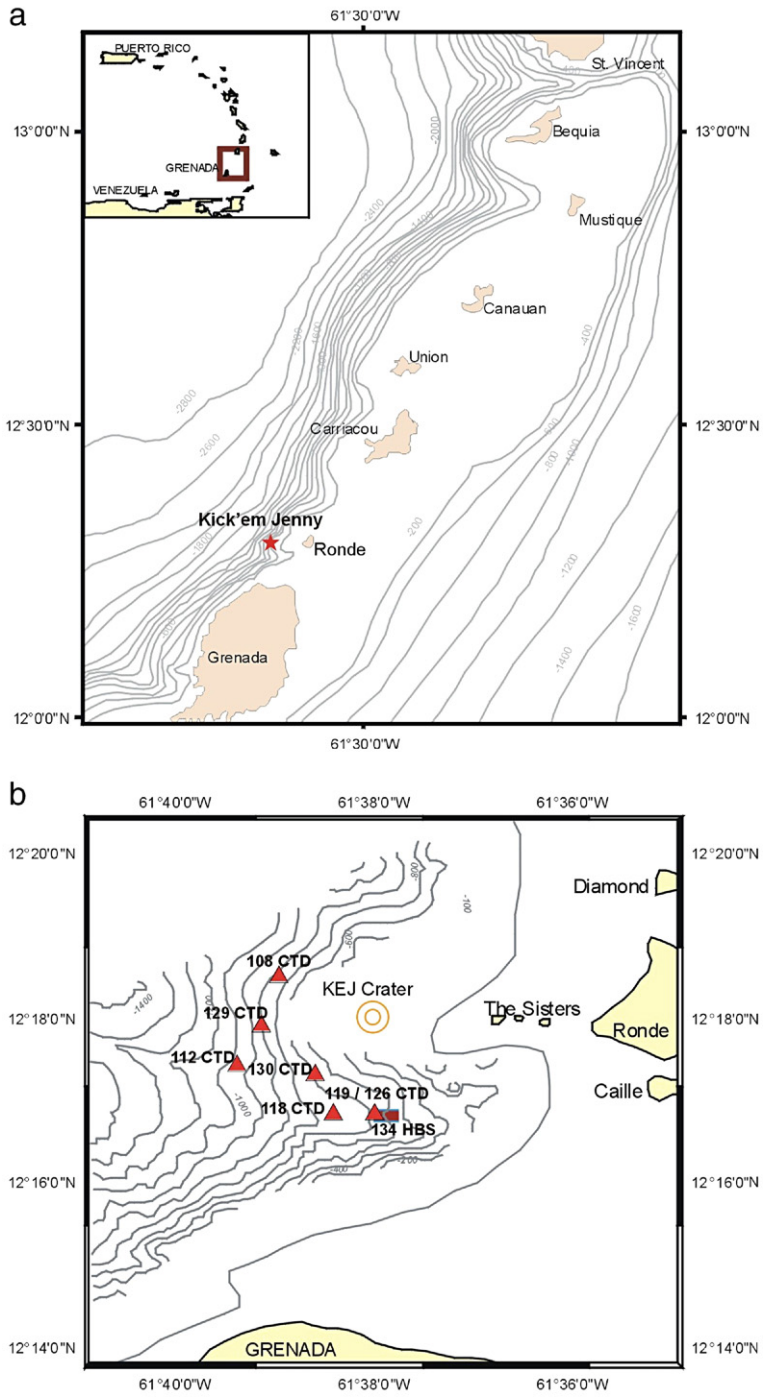

Fig. 1. a. Map of the working area. b. Locations of sampling stations along the western and southern flanks of the Kick'em Jenny submarine volcano (all stations are CTD/water-column profiles, except 134 HBS, which is the location of the bottom fluid sampling).

KeJ volcano is the only known active submarine volcano of the Lesser Antilles island arc and is located at 12°18′N and 61°38′W, ~9 km north of the island of Grenada, near the steep western flank of the arc (Fig. 1a,b). The volcano summit shoals to 178 m below sea level with the floor of the crater having a maximum depth of 284 m below sea level (Watlington et al., 2002). The crater is located at the summit of an asymmetrical

cone, which rises about 1300 m from the seafloor on its western site. The eastern flank shoals towards the Grenadine platform. Detailed investigations in 2002 had shown that hydrothermal venting occurred in the inner crater, which may have been the location of recent volcanic activity (Koch et al., 2002). Twelve eruptions have been reported for KeJ since 1939, with the eruptions reaching the sea surface in 1939, 1974, and 1988 (Lindsay et al., 2005). The other eruptions were detected from seismic activity, with the last eruption reported in 2001. The summit of KeJ is probably located within what appears to be the remnant of much larger volcano, which has been mapped during a high-resolution bathymetric survey (Shepherd, 2004). Recent volcanic activity at KeJ was further confirmed by a high-resolution bathymetric survey that showed changes in the morphology of the volcanic edifice when compared to previous surveys (Watlington et al., 2002). The eruptions at KeJ are characterized by alternating effusive and explosive volcanism. Pyroclastic material and breccias containing massive basaltic lava rocks have been observed.

The surface of the western flank of KeJ is characterized by fresh volcanic sand containing small rock fragments and mafic minerals, overlain by a thin hemipelagic sediment layer. Water-column profiles were obtained above the western and southern flanks of KeJ (Fig. 1b). Direct fluid sampling on the ocean floor was carried out in a flat area at the base of the southern flank, between depths of 542 m and 712 m (i.e., Caille valley). Ocean floor observations using a towed TV and photo camera sledge in this region showed coarse-grained tephra overlain by a thin sediment layer of variable thickness, cut by several small faults.

3. Samples and methods

Water-column surveys were done using a standard CTD (conductivity–temperature–depth) probe (Seabird 911) with a rosette water sampler equipped with twenty-four 10 L Niskin bottles. The "Hydro Bottom Station" (HBS), a lander system designed for sampling diffuse hydrothermal fluids (Halbach et al., 2001), was used to recover samples near the seafloor on the flanks of the volcano. The samples were pumped into Teflon bags through a mobile hydrolance that can be positioned between 0 and 60 cm above the seafloor. Six samples were taken at sediment-covered sites between 542 and 712 m. No focused-flow fluids (e.g., chimneys) were observed. The samples collected were diffuse-flow, low-temperature fluids that produced shimmering water.

Only samples taken by the HBS close to the seafloor were filtered (0.2 μm). Samples for trace-metal analyses were acidified to pH = 2 with Suprapure (Merck) HCl. After onboard measurements of pH, Eh, sulfide, trace metals by voltammetry and CH_4 by gas chromatography were completed, the samples were stored for analysis back in shore-based laboratories. An overview of the methods and equipment used is given in Table 1. Detailed descriptions and references on the methods used in the analysis of the major, minor and trace elements, and gas analyses, can be found in Koschinsky et al. (2002).

Stable isotope measurements were done using a H_2 equilibration method for D/H values and a CO_2 equilibration method for $^{18}O/^{16}O$ values with a Finnigan MAT Delta-S mass spectrometer. After equilibration (120 min for the hydrogen isotopes and 400 min for the

Table 1
Overview of analytical methods used onboard and in the home laboratories

Analyte	Method, equipment	Determination limit	Standard deviation
SiO_4, Cl, SO_4	Photometry, Technicon Auto Analyzer	0.5 mmol/kg	1–2%
S^{2-}	Stripping voltammetry, Metrohm	0.003 μmol/kg	5%
Na, K	Flame photometry, Eppendorf ELEX	0.25 μmol/kg	2%
Li	Flame AAS, Perkin Elmer AAS 5000	2 μmol/kg	3%
Ca, Mg	Flame AAS, Perkin Elmer AAS 5000	0.25 mmol/kg	2%
Fe, Mn	Stripping voltammetry, Metrohm	10 nmol/kg	≤8%
Zn, Cu, Ni	Stripping voltammetry, Metrohm	4 nmol/kg	≤7%
Pb, Cd, Co	Stripping voltammetry, Metrohm	0.5–0.8 nmol/kg	≤10%
V, U, Mo, Cr	Stripping voltammetry, Metrohm	1–5 nmol/kg	5%
As, Sb, Se	Stripping voltammetry, Metrohm	0.3–4 nmol/kg	5–10%
DIC	Coulorimetric titration	100 μmol/kg	0.1%
DOC	Catalysed high temperature oxidation-IRD, DIMA-TOC 100	10 μmol/kg	10%
CH_4	Purge and trap-GC–FID/vacuum ultrasonic stripping-GC–FID	0.05 nmol/kg	10%
He, Ne	Mass spectrometry		0.4%
$\delta^{13}C$–CH_4	GC–C–IRMS, Finnigan DeltaPlusXL	4 nmol/kg	0.7‰
δD, $\delta^{18}O$	Finnigan MAT Delta-S mass spectrometer		0.8/0.1‰

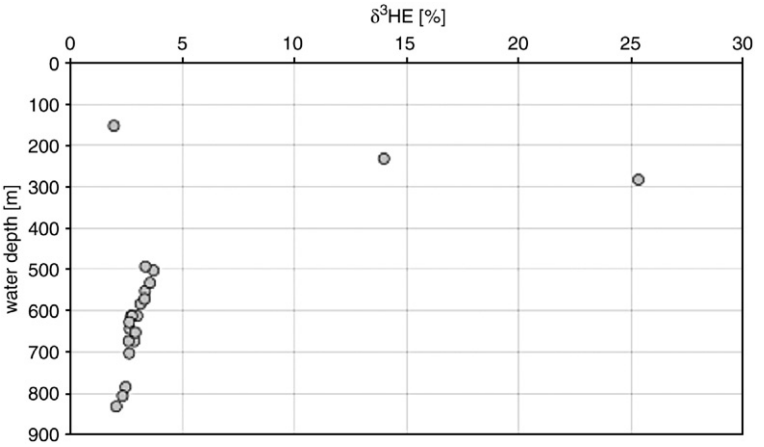

Fig. 2. Helium isotopic ratios in the water column, measured in samples from stations 108 CTD, 112 CTD, and 130 CTD. The high δ^3He values between 200 and 300 m water depth indicate a primordial mantle component in fluids emanating from the crater.

oxygen isotopes) ten measurements were carried out on each sample. δD and δ^{18}O values were calculated using ISODAT™ and reported in the standard δ notation representing per mil deviation relative to VSMOW (Vienna Standard Mean Ocean Water). Details on the instrumentation, calibration, and the measurement methods are given in Meyer et al. (2000).

4. Results

4.1. Helium

The isotopic signature of He provides information on the source of the hydrothermal solutions, which can contain mantle and/or crustal components. An increase in the δ^3He value (where $\delta^3\text{He}\ (\%) = R_{\text{sample}}/R_{\text{atmosphere}} - 1) * 100$ and $R_{\text{atmosphere}} = {}^3\text{He}/{}^4\text{He}_{\text{atmosphere}} = 1.384 * 10^{-6}$), relative to the atmospheric standard, indicates a mantle component.

Increased values of δ^3He up to 25.3% were found in the water-column profiles within the depth range 200–300 m (Fig. 2). However, no significant increase in δ^3He values was observed over the depth range of 500–650 m where hydrothermal anomalies such as increased CH_4 and trace-metal concentrations (see Sections 4.2 and 4.4 below) were found. The reported depth of the crater floor (284 m, Watlington et al., 2002) is similar to the depth of our maximum values of δ^3He (300 m), suggesting that the shallow hydrothermal signals most likely originate from within the crater. However, the large sampling intervals (100, 200, and 300 m) of our He samples do not allow a better resolution of the exact depth of hydrothermal fluid discharge, therefore we might have missed the maximum δ^3He value between 200 and 300 m.

4.2. Methane

Methane concentrations of up to 14 nM were measured in the water-column profiles, where background concentrations are around 2 nM (Fig. 3). In the shallow depths of around 300 m, where the He isotopic anomaly was observed in samples from stations 108 CTD and 112 CTD (Fig. 2), only a slight increase in CH_4 was measured for these same samples (Fig. 3), which is not considered to be significant. The CH_4 maxima occur in a water depth range of 550–650 m. Thus it is interesting to note that there is a clear He signal from the summit area with no corresponding CH_4, and by contrast there are CH_4

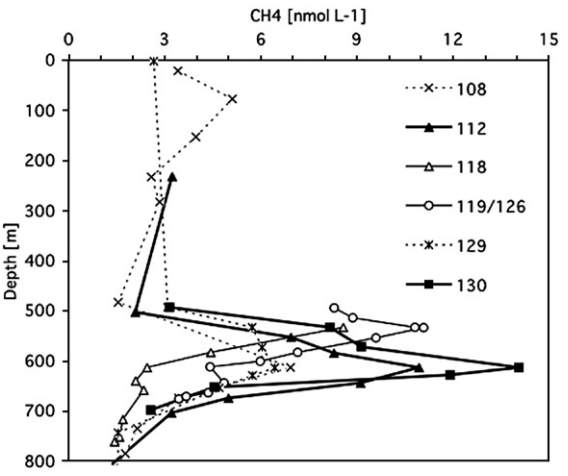

Fig. 3. Methane concentrations in all CTD profiles, indicating the existence of two CH_4-rich zones: one maxima occurs around 540 m depth and another at 615 m.

anomalies from the volcano flank sites with no significant He input. Closer inspection of the depth profiles for CH_4 shows the possible presence of two plumes between 550 and 650 m (Fig. 3). The highest CH_4 concentrations were found along the SW side of the volcano at a depth of 615 m (stations 112 CTD and 130 CTD), while to the south the maximum is located at 540 m depth (stations 118 CTD and 119/126 CTD). This is consistent with the results for the trace metals (see Section 4.4). The stations located further to the north (129 CTD and 108 CTD) show a broader peak with lower maximum values, indicating that they are probably located at a greater distance from the hydrothermal source. Another explanation would be that there is just one source and advection of the plume around the summit of the volcano produces different plume heights. However, considering the different trace-metal chemistry in the two plume levels (see Section 4.4), we favor the first explanation. In the near-bottom HBS samples, concentrations of CH_4 between 18.4 and 22.1 nM (Table 2) were measured.

Selected CH_4 samples were analyzed for their carbon isotopic $\delta^{13}C$ values, with results ranging between −45 and −51‰. A significant increase of the ^{13}C contents was observed for CH_4-rich samples between 550 and 650 m water depth.

4.3. DIC and DOC

DIC (dissolved inorganic carbon) concentrations in the water-column samples range between 2160 and 2220 μM and are within the range measured at other locations along the island arc (R. Seifert, unpublished data). Only one high value, 2366 μM, was measured in one sample of station 130 CTD, from a depth of 653 m.

At two stations (108 CTD and 112 CTD), DOC (dissolved organic carbon) was analyzed in the water-column samples. At both sites the DOC profiles correlate with the CH_4 profiles, with maxima of 125 and 115 μM DOC, respectively, over the same depth intervals (Fig. 4). No data for DOC are available from stations 118 and 119/126.

4.4. Major and minor elements and trace metals

Water-column chemical profiles at the various stations showed high variability in trace-metal concentrations, with numerous indications of hydrothermal input into the water column. As the samples were not filtered, the data represent the total dissolvable (at pH 2) concentrations of the respective elements. The shallow hydrothermal plume characterized by the He data is positively correlated with significant increases in the concentrations of Fe, Zn, and U between 250 and 300 m, with minima for Mo and V at the same depth interval at station 108 (Fig. 5). Other metals, including Mn, Cu, Cd, Pb, Ni, and Co do not show obvious anomalies in the water samples from this station.

Significant trace-metal anomalies were also found in the depth range 530 to 650 m. For example, significant increases in metals such as Cu, Cd, Ni, Pb, and Zn were noted in some samples (e.g., see 650 m water depth at station 118 CTD, Fig. 6). Most trace-metal profiles do not correlate with the CH_4 profiles at these stations. For example, at station 129 CTD the CH_4 maximum ranges around 600 m depth, while Zn, Cu, V, and U show a minimum at this depth and have two maxima above (at 533 m depth) and below (at 650 m depth; Fig. 7). In profile 118 CTD there is trace-metal maximum at 650 m depth, while CH_4 is low at 650 m depth although rises significantly above 550 m.

Table 2
Major, minor and trace element data for the six bottom fluid samples collected on the SW flanks of the Kick'em Jenny volcano in comparison with average background seawater concentrations measured in the water-column profiles in the depth range 500–700 m

Sample	Depth (m)	SO_4^{2-} (mM)	Cl (M)	Si (mM)	Na (M)	Ca (mM)	Mg (mM)
134 HBS 1	542	29.3	0.535	0.254	0.417	9.13	51.0
134 HBS 3	550	30.1	0.535	0.221	0.435	9.63	52.3
134 HBS 4	566	30.8	0.531	0.193	0.443	10.0	53.1
134 HBS 7	600	25.9	0.476	0.332	0.426	8.75	51.0
134 HBS 9	712	28.1	0.506	0.279	0.423	9.00	51.0
134 HBS 10	652	28.9	0.528	0.239	0.430	9.25	51.4
Seawater	500–700	30.3	0.563	0.192	0.460	10.8	54.9

Sample	As (nM)	Cd (nM)	Cu (nM)	Fe (nM)	Mn (nM)	Mo (nM)	Ni (nM)
134 HBS 1	57	0.9	26	15.9	<10	107	163
134 HBS 3	44	1.7	30	16.4	12.7	107	239
134 HBS 4	49	3.6	22	23.2	<10	102	166
134 HBS 7	109	1.7	22	27.7	<10	93	132
134 HBS 9	51	1.0	34	14.6	10.0	87	155
134 HBS 10	48	0.9	28	10.7	<10	104	163
Seawater	20	0.9	8	10.0	<10	110	9.4

Sample	Pb (nM)	Sb (nM)	U (nM)	V (nM)	Zn (nM)	CH_4 (nM)
134 HBS 1	0.5	0.82	12.1	18.9	156	20.3
134 HBS 3	1.7	0.82	12.7	12.3	192	
134 HBS 4	0.5	0.49	11.9	16.1	183	20.2
134 HBS 7	1.1	0.33	10.0	18.2	218	
134 HBS 9	0.5	0.41	10.9	15.6	180	22.1
134 HBS 10	1.6	0.74	10.8	17.0	215	18.4
Seawater	0.5	2.05	12.7	20.0	21	2.0

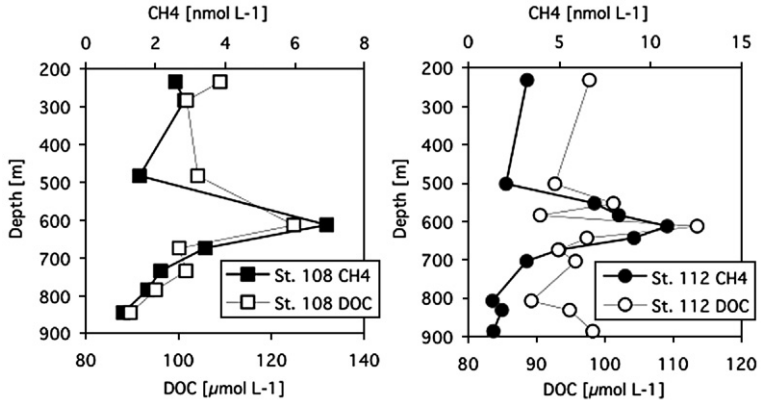

Fig. 4. DOC concentrations at stations 108 CTD and 112 CTD that mimic the profiles of CH_4 at these stations.

Considering the evidence for high concentrations of trace metals in the depth range of 500–700 m, bottom-water sampling with the HBS was restricted to these depths at the flanks of the volcano (see Fig. 1b). As we were unable to sample the summit directly, the study was restricted to the deeper vent sites where there was still good evidence for hydrothermal emissions. Six samples were collected from different locations between 542 and 712 m and all confirm the hydrothermal input observed in the water-column profiles, although pH and Eh values measured onboard did not show a significant deviation from background values. In these samples, concentrations of the major species such as Cl, SO_4, Mg, Na, and Ca are depleted by up to about 20% when compared to ambient seawater values (Table 2). By contrast, Si concentrations were found to be up to 65% higher. Also, many trace metals that are typically enriched in hydrothermal fluids (e.g., Zn, Cu, Ni, and As) have higher concentrations in the bottom-water samples over ambient seawater (Table 2). Zinc and Ni showed

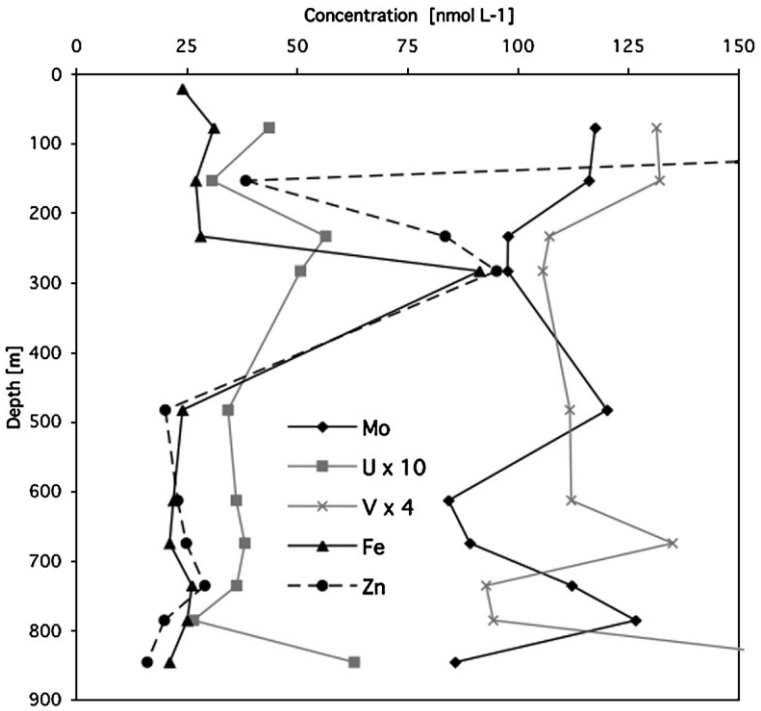

Fig. 5. Water-column profiles of select trace metals at station 108 CTD, consistent with a shallow hydrothermal source around 300 m depth.

the most elevated concentrations, up to about 0.2 μM, which is consistent with the enrichment of these elements noted in the water-column surveys. Other elements, such as Mo, U, V, Sb, and Se, were found to be slightly depleted in the bottom fluids (Table 2). No dissolved sulfide was detected in the KeJ fluids with all values < 0.3 μM.

4.5. Oxygen and hydrogen isotopic data

Oxygen and hydrogen isotope ratios were analyzed for the six bottom fluid samples collected with the HBS, and one sample at 674 m from station 108 CTD (Fig. 8) for comparison. In order to determine the influence of meteoric water on the fluid samples, if any, our data were compared to literature data for meteoric water from the region. Meteoric water from Grenada (data from Taylor, 1997, Fig. 6.3 therein) has a $\delta^{18}O$ of about −2‰ and a δD of about −6‰ on the Global Meteoric Water Line (Craig, 1961). The background sample of station 108 CTD lies close to standard mean ocean water (VSMOW). The six HBS samples are shifted slightly towards higher $\delta^{18}O$ and δD values. This shift cannot be explained by mixing of meteoric water with negative values (irrespective of using the Global Meteoric Water Line or the Local Meteoric Water Line of Barbados) and ambient seawater of station 108 CTD.

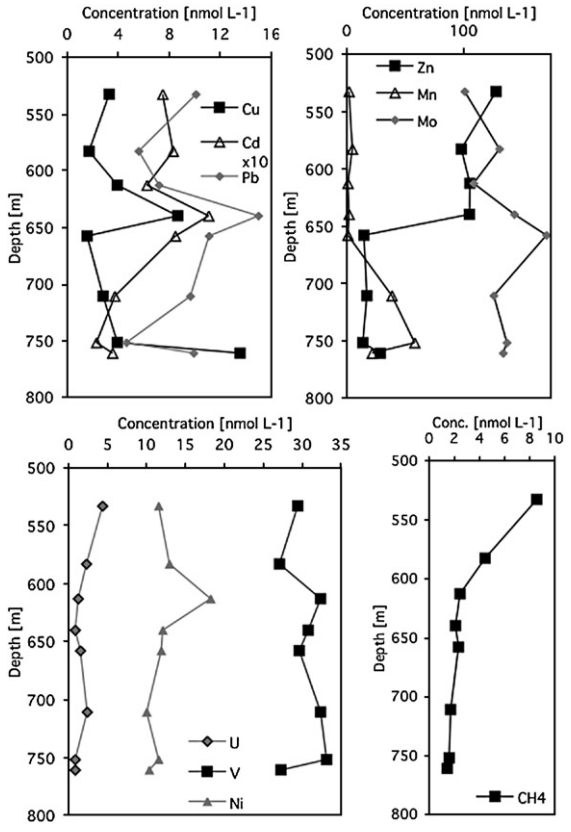

Fig. 6. Water-column profiles of trace metals and CH_4 at station 118 CTD (southern flank of Kick'em Jenny), showing evidence for hydrothermal discharge at 600–650 m water depth.

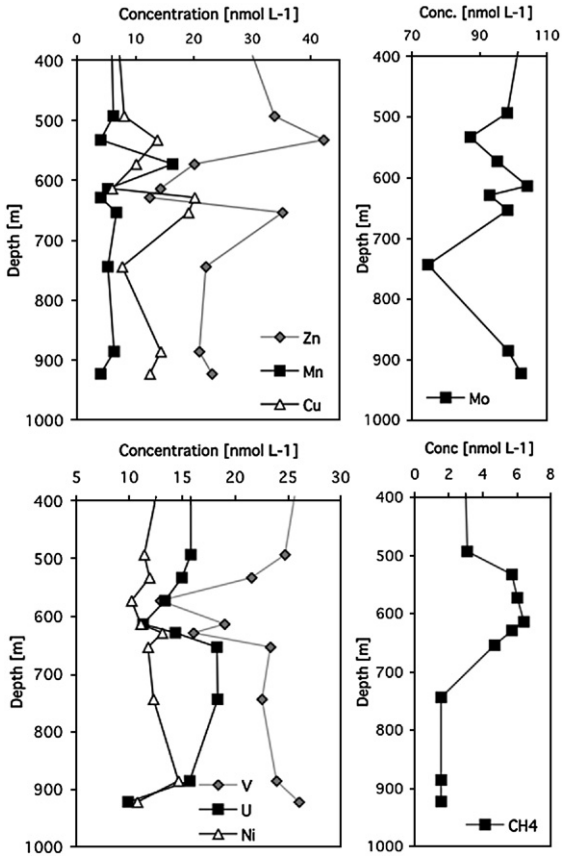

Fig. 7. Water-column profiles of trace metals and CH_4 at station 129 CTD (western flank of Kick'em Jenny), showing metal-rich and metal-poor layers in the hydrothermal plume between 500 and 700 m depth.

5. Discussion

5.1. Helium

The shallow-water He anomaly observed around 300 m depth is likely related to hydrothermal venting observed in the volcanic crater during a cruise after our CARIBFLUX cruise (Wishner et al., 2005), and indicates a mantle source for this component. Unfortunately, we were not able to directly compare bottom-water analyses for this summit vent field with those from the flanks vents of the volcano. However, the noticeable He signal would suggest that this shallow plume represents a more active, possibly focused

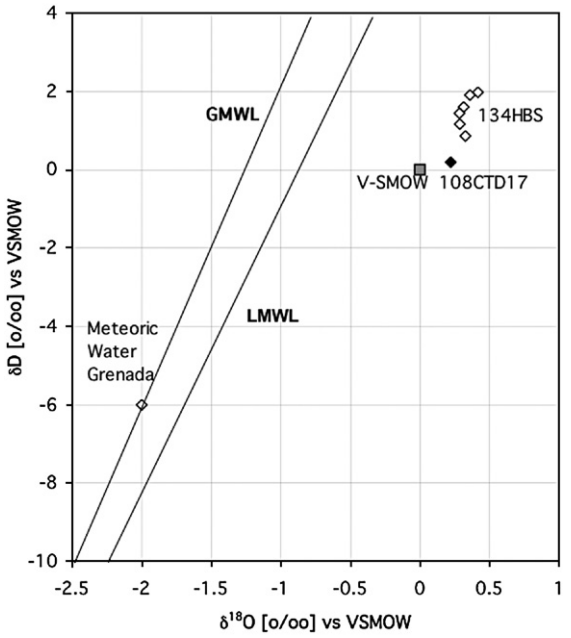

Fig. 8. Oxygen and hydrogen isotopic ratios (δ^{18}O and δD) for the bottom fluid samples of station 134 HBS and the water-column sample 108 CTD 17. The plot shows that the bottom fluids are not a mixture of seawater and meteoric water, but rather a mixture of seawater and hydrothermal fluid. Shown for comparison is the Vienna Standard Mean Ocean Water (VSMOW) and meteoric water of Grenada; the Global Meteoric Water Line (GMWL) is defined after Craig (1961). The data source for the Local Meteoric Water Line (LMWL) for Barbados (data found closest to Grenada) is http://isohis.iaea.org/GNIP.asp.

venting site, than the deeper sites, which are obviously weak, diffuse sources. Even so, published δ^3He values for plumes from other arc volcanoes range between 24 and 181% (de Ronde et al., 2001; 2005), thus the shallow KeJ plume with δ^3He value of 25% is either still not a particularly active field, and/or the distance the samples were collected away from the likely source in the crater meant they were significantly diluted.

In the depth range of the observed CH_4 and trace-metal anomalies (500–700 m), δ^3He values of <4% being only slightly enhanced compared to the background of about 2% provide no corroborating evidence of a magmatic component in the hydrothermal fluids responsible for the elevated CH_4 and trace-metal concentrations (Fig. 2). Thus we suggest that the hydrothermal activity that produces the venting on the flanks of the volcano around 600 m depth either does not contain a significant primordial mantle component. Alternatively, we do not see the mantle component due to the fact that these are dilute, diffuse fluids, with CH_4 and metals secondarily added.

5.2. Carbon compounds: methane and DOC

The much smaller size of CH_4 anomaly at the shallow depth range around 300 m compared to the large He signal suggests a CH_4-poor and He-rich source. It also might, though less likely in view of the sampling location directly at the KeJ, indicate a greater distance of the source from the sampling points so that only the signals from the chemically and biologically inert noble gases can be found at higher concentrations. Moreover, enhanced CH_4 concentrations in the upper water column above 500 m might be caused by biological in-situ production of CH_4, especially in areas of high primary productivity (Lamontagne et al., 1973; Karl and Tillbrook, 1994; Scranton and Brewer, 1977; Seifert et al., 1999). However, similar observations of poor correlation between CH_4 and He were made in other back-arc settings as the Mariana back-arc (Horibe et al., 1986), the Sangihe and Talaud ridges (Belvisto et al., 1987), and the southern Kermadec arc (de Ronde et al., 2005). These findings imply that origins of the dissolved CH_4 distinct from the deep crustal component are more likely from organic matter of the upper sub-seafloor.

Investigation of the carbon isotopic composition of CH_4 shows a significant increase of the δ^{13}C values with increasing CH_4 concentrations, and does not support a biogenic (microbial methanogenesis) origin of the CH_4, which would produce the opposite trend. Rather, the data suggest a dominance of thermogenic CH_4 from hydrothermal alteration of sedimentary organic matter (Whiticar, 1999). This assumption is also supported by the enrichment of DOC in the CH_4 plume. The CH_4 concentrations in the water column therefore appear to be mainly controlled by the mixing of CH_4-rich hydrothermal fluids and CH_4-poor seawater rather than by the microbial degradation of CH_4 in the water column. The high DOC concentrations in the water column and their correlation with the CH_4 data may indicate an increase in biological/microbiological activity in the CH_4-rich horizon. It may also be related to the interaction of the fluid with the sediment through which it is percolating.

5.3. Major and minor elements and trace metals

Trace-metal anomalies for Fe and Zn in the water-column profile of station 108 CTD around 300 m (Fig. 5) correlate with high δ^3He values (Fig. 2), suggesting a strong hydrothermal source for these metals. Very high Zn concentrations of up to 366 nM in the surface layer probably derive from surface input. The relatively clear signal for Fe and Zn, implies that the source is not a

diffuse one, but probably a focused source of higher temperature. Low Cu concentrations can be explained by the strong temperature control of Cu solubility in hydrothermal systems, which strongly decreases below 350 °C (Metz and Trefry, 2000). However, hydrothermal solutions cannot get that hot at such shallow depths. That is, the two-phase curve for seawater (Bischoff and Rosenbauer, 1988) suggests that vent fluid temperatures on the crater floor cannot exceed ~235 °C if boiling was to occur at 300 m depth, where the δ^3He plume maximum was found.

The variable concentrations of trace metals in the depth range 530–650 m (Figs. 6 and 7), in part inversely correlated with the CH_4 anomalies, may indicate emanation of different types of hydrothermal fluids, such as a metal-depleted gas-rich vapor phase and a gas-depleted metal-rich brine phase resulting from phase separation in the sub-surface (see vapor and brine phase data in Butterfield and Massoth, 1994). However, as we have no information on the exact source of the venting on the flanks and on the temperatures of these fluids, this interpretation has to be considered with care. Increased concentrations of some metals in some profiles close to the seafloor at 760 m depth may also be related to re-suspension of bottom sediments. In summary, our results indicate He-, Fe- and Zn-rich venting probably of high temperature at the summit of the volcano and diffuse venting at the flanks, with different plume chemistry. Both data are in agreement of data from the Brothers volcano (southern Kermadec arc; de Ronde et al., 2005) where Fe-rich plumes were located both above a cone growing out of the caldera of the volcano and another site on the inside of the caldera walls, both having very different chemistries.

The distribution of trace metals in the diffuse bottom fluids (Table 2) is reasonably consistent with similar signals in the water-column profiles (Figs. 5, 6 and 7). The high Zn concentrations of up to 218 nM, which exceed the concentrations of all the other metals measured, agree with high Zn concentrations compared to ambient seawater measured in the region around Guadeloupe by Polyak et al. (1992). High Zn concentrations of up to 3.1 μM where also reported for fluids from vent sites in back-arc areas, when compared to MOR fluids (maximum 0.78 μM, see compilation of von Damm, 1995). Elevated Zn and Pb concentrations in hydrothermal fluids and massive sulfides of back-arc basin systems are considered to be the result of hydrothermal alteration of felsic volcanic rocks and/or sedimentary rocks (e.g. Manus basin; Stanton, 1994). When compared to MOR vent fluids, where concentrations of several hundred μM have been measured for metals such as Fe, Mn, Cu, and Zn (von Damm, 1995), the concentrations of the KeJ bottom samples are significantly lower. In particular, the low concentrations of Fe and Mn are in contrast to most MOR vent fluids, where typically Fe and Mn are the most enriched heavy metals, with Fe often reaching mM concentrations in the end-member fluid. However, the diffuse fluids of the KeJ have probably undergone some chemical modification during cooling and mixing with seawater. The low Fe concentrations can be explained by precipitation of Fe sulfides or oxides in the sub-surface. The depletion of Mo, U, V, Sb, and Se in the bottom fluids (Table 2) is well known from MOR hydrothermal fluids and is explained by the fixation of these elements in solid phases such as sulfide minerals (Metz and Trefry, 2000). The high pH may be related to interactions of the fluids with the sediment, as has been observed in the Guaymas Basin where values of high pH were explained by the dissolution of carbonate and the addition of ammonium from thermocatalytic cracking of planktonic carbon (von Damm, 1985) or simply because of dilution with seawater. Similar fluid–sediment interactions have also been observed in the Okinawa Trough (Ishibashi et al., 1995).

The fluids taken from the seafloor are not pure hydrothermal end-member fluids, but are a mixture of hydrothermal fluid and ambient cold seawater. The most commonly used method is to extrapolate from the mixed fluid data to the hydrothermal end-member via the concentration of Mg, which is normalized to Mg=0. Pure hydrothermal fluids are assumed to be Mg-free due to its removal from heated seawater and precipitated as alteration products at temperatures above about 150 °C (e.g., Mottl and Holland, 1978). Another method is to calculate the end-member concentration on the basis that the end-member fluid has a sulfate concentration of zero, a feature also commonly observed in hydrothermal fluids, especially those at MORs. This is due to the precipitation of anhydrite ($CaSO_4$) at temperatures of about 150 °C (Mottl and Holland, 1978). However, studies of arc-related hydrothermal vent fluids have shown that sulfate may be added to these fluids from hydrothermal sources (e.g., Gamo et al., 1997; de Ronde et al., 2005); thus, back-calculation of the vent fluid compositions via a regression through $SO_4=0$ may not be valid. Both calculations resulted in hydrothermal fluid components of up to 15% in the HBS samples. However, extrapolation of some of the Cl data on this basis resulted in negative end-member values. Thus, it is possible that end-member calculations using these methods is not feasible here because the Mg and SO_4 concentrations of the fluids have been altered by subsequent reactions with the sediment, or there have been acid sulfate fluids being expelled from the vents, as

is commonly seen at sites along the Kermadec and Mariana arcs. For example, model calculations have shown that on the flanks of the Juan de Fuca Ridge organic matter degradation in the sediment via sulfate reduction is an additional sink for sulfate (Giambalvo et al., 2002). Therefore, only a rough estimate can be made on the contribution of hydrothermal fluid in the samples. Nevertheless, the KeJ end-member fluid must have a significantly lower chlorinity (probably less than 50%) than ambient seawater; this cannot be explained by water–rock interactions or precipitation of Cl-bearing phases. A more likely explanation is phase separation, i.e. boiling in the sub-surface, with the fluids sampled representing the condensed vapor phase diluted with ambient seawater.

5.4. Oxygen and hydrogen isotopic data

The isotopic data for O and H in the bottom-water samples from the flanks of the volcano cannot be explained by intrusion of meteoric water from the basement of the island of Grenada, as was shown by the comparison with the meteoric water line (see Section 4.5). Values for $\delta^{18}O$ and δD of the diffuse samples from the flanks of the KeJ are both greater than VSMOW. Hydrothermal fluids generally have higher $\delta^{18}O$ values as a result of isotopic exchange with silicate and carbonate country rocks that generally have $\delta^{18}O$ values higher than +5.5 (Taylor, 1997). The $\delta^{18}O$ values of our samples range between +0.3 and +0.45‰. Jean-Baptiste et al. (1997) reported $\delta^{18}O$ values of 0.53–2.3‰ for MOR vent fluids from different tectonic settings, which is close to the range of our data and is considered a result of fluid/rock interaction.

Hydrogen isotope ratios of vent fluids with a range in Cl concentration show considerable variability (Shanks et al., 1995; Berndt et al., 1996). Hydrogen isotope fractionation is relatively insensitive to water–rock reactions because the rocks contain little H compared to the water. However, during sub-critical phase separation the isotopic fractionation depends on both temperature and salinity (Horita et al., 1995). High δD values have been described from low chlorinity fluids that underwent phase separation at shallow levels in the oceanic crust (Shanks et al., 1995; Berndt et al., 1996). Phase separation during adiabatic decompression, i.e., pressure release during fluid ascent, produces vapors with positive δD values (Shanks et al., 1995). Experiments of Driesner and Seward (2000) showed that the strongest D fractionation into the vapor phase occurs between about 270 and 350 °C. Assuming that at the KeJ site phase separation takes place approximately at the depth of the fluid emanations, around 600–700 m, or possibly below that in the sub-seafloor, the boiling temperature of these fluids would be around 280 °C (based on the two-phase boundary for seawater, Bischoff and Rosenbauer, 1988), with the emanating fluids being a strongly diluted form of the end-member fluid. This could explain the relatively high δD values of our samples (measured data range up to +2‰, with end-members probably being higher) compared to literature data for samples from depths greater than 2000 m (up to 4.1‰; Shanks et al., 1995). Our H isotope data therefore may indicate that at the KeJ site phase-separated fluids emanate into the surrounding seawater and that the sampled fluids represent a condensed vapor phase mixed with seawater. This is consistent with the reduced concentrations of some major ions compared to ambient seawater. With a magmatic input into the system we might expect more negative δD values, which is not evident in our samples from the flanks of KeJ at least.

6. Conclusions

Hydrothermal discharge into the water column is evident from both the summit crater whose floor is at 300 m, and on the flanks of the Kick'em Jenny volcano (500–700 m). Near the summit, there are indications from He isotopes and some trace metals of a strong, probably focused source, similar to results from surveys of plumes along the Kermadec arc (de Ronde et al., 2001) that show hydrothermal activity associated with arc volcanoes occurs mostly at, or near, their summit. Unfortunately, restrictions imposed on us due to possible hazards did not allow us to sample within the crater region. A significant hydrothermal input of CH_4, DOC and trace metals over the flanks of the volcano, between 500 and 700 m water depth, was also found. As only diffuse flow through sediment was observed, the fluids emanating on the seafloor appear to be of relatively low temperature. However, we believe that these fluids were originally hot fluids with temperatures of up to 280 °C, as the chemical data indicate that the fluids sampled at the bottom are vapor-phase fluids likely resulting from phase separation that later mixed with ambient seawater during their ascent.

Magnesium and SO_4 data indicate that the sampled diffuse fluids probably contain only a few percent of the hydrothermal end-member fluid. The lack of a temperature anomaly might also imply conductive cooling of the fluids. This would require a long residence time of the fluids in the sub-surface, possibly related to a high porosity of the country rock, or due to the slow percolation of the fluid through the sediment layer. The

relatively high pH, high DOC and low concentrations of some transition metals and sulfide indicate an interaction of the fluids with the sediment. We suggest that most of the sulfide and a large part of the original metal content of the fluid may have precipitated in the sub-surface. This assumption is supported by indications of sub-seafloor boiling, which effectively removes any metals from the hydrothermal fluids prior to them being expelled on the seafloor.

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