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Carbon release from submarine seeps at the Costa Rica fore arc: Implications for the volatile cycle at the Central America convergent margin

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[1] We report total dissolved inorganic carbon (DIC) abundances and isotope ratios, as well as helium isotope ratios ($^3He/^4He$), of cold seep fluids sampled at the Costa Rica fore arc in order to evaluate the extent of carbon loss from the submarine segment of the Central America convergent margin. Seep fluids were collected over a 12 month period at Mound 11, Mound 12, and Jaco Scar using copper tubing attached to submarine flux meters operating in continuous pumping mode. The fluids show minimum $^3He/^4He$ ratios of 1.3 R_A (where R_A is air $^3He/^4He$), consistent with a small but discernable contribution of mantle-derived helium. At Mound 11, $\delta^{13}C_{\sum CO2}$ values between −23.9‰ and −11.6‰ indicate that DIC is predominantly derived from deep methanogenesis and is carried to the surface by fluids derived from sediments of the subducting slab. In contrast, at Mound 12, most of the ascending dissolved methane is oxidized due to lower flow rates, giving extremely low $\delta^{13}C_{\sum CO2}$ values ranging from −68.2‰ to −60.3‰. We estimate that the carbon flux (CO_2 plus methane) through submarine fluid venting at the outer fore arc is 8.0×10^5 g C km^{-1} yr^{-1}, which is virtually negligible compared to the total sedimentary carbon input to the margin and the output at the volcanic front. Unless there is a significant but hitherto unidentified carbon flux at the inner fore arc, the implication is that most of the carbon being subducted in Costa Rica must be transferred to the (deeper) mantle, i.e., beyond the depth of arc magma generation.

1. Introduction

[2] Subduction zones represent the major avenues for geochemical cycling between Earth's major external reservoirs (the oceans, sediments and oceanic/continental crust) and Earth's interior, i.e., both shallow and deep mantle. Water and other volatiles (e.g., carbon, nitrogen, and sulfur), released from the subducting crust and sediments as the oceanic lithosphere descends into the mantle and experiences progressively higher pressures and temperatures, control fundamental processes in the subduction zone. At shallow levels, the water and carbon fluxes influence the formation and destruction of gas hydrates, and support chemosynthetic vent communities in the outer fore-arc region [*Judd and Hovland*, 2007; *Judd*, 2003]. At greater depths, excess pore fluid pressures reduce the strength of faults and may control the updip limit of the seismogenic zone [e.g., *Byrne et al.*, 1988; *Moore and Saffer*, 2001; *Ranero et al.*, 2008]. Deeper still, volatiles released from the subducting slab may serpentinize the overriding plate and promote the generation of hydrous partial melts in the mantle wedge [*Tatsumi and Eggins*, 1995]. Finally, any volatiles that are not lost by fluid flow, dehydration, decarbonation reactions and/or magma generation at the volcanic front will be carried into Earth's deep mantle.

[3] The fate of carbon during subduction zone processes is a poorly known component of Earth's natural carbon cycle. Estimates of the total carbon flux associated with volcanism at the Central America volcanic front have shown that the output flux is only 12%–18% of the carbon which is potentially available by input via the trench [*Hilton et al.*, 2002; *Shaw et al.*, 2003; *de Leeuw et al.*, 2007]. This result indicates that either carbon is efficiently recycled to the (deeper) mantle, i.e., the mantle beyond the zone of arc magma generation, or significant losses of carbon occur in the fore-arc or back-arc regions. Significantly, thermodynamic modeling by *Gorman et al.* [2006] predicts efficient release of CO_2 from the top of the subducting slab at relatively shallow depths (i.e., between ~65 and 80 km depth) beneath the fore arc

in Central America, and *de Leeuw et al.* [2007] argued that subducted sediments do not represent a direct source of CO_2 to the back-arc region. Therefore, direct measurements of volatile fluxes and compositions in the fore-arc region are critical for completing the carbon mass balance for the Central America convergent margin. The numerous submarine fluid venting sites offshore Nicaragua and Costa Rica are obvious targets for assessing the carbon flux at the outer fore-arc region.

[4] In this contribution, we report the dissolved volatile characteristics of well-mapped fluid venting sites (Mound 11, Mound 12, and Jaco Scar (Figure 1)) at the submarine segment of the Costa Rica fore-arc margin. Measurements of ^{3}He/^{4}He ratios and $\delta^{13}C_{\sum CO2}$ values are used to assess the provenance of dissolved helium and carbon, respectively, dissolved in the seep fluids. In addition, through use of an innovative sampling approach coupling copper sampling coils to submarine flux meters [*Tryon et al.*, 2001; *Füri et al.*, 2009], we evaluate the extent of temporal variability in the volatile characteristics over a 12 month period. The observed DIC abundances, together with previous estimates of methane fluxes [*Mau et al.*, 2006], allow limits to be placed on the total flux of carbon (CO_2 plus methane) released via submarine fluid venting at mound structures at the Costa Rica outer fore arc. This flux estimate represents an important element of the total fore-arc flux and provides essential input to help complete the carbon mass balance for the Central America convergent margin.

2. Geologic Setting and Background

[5] At the Costa Rica margin, the Cocos Plate subducts beneath the Caribbean Plate at a convergence rate of ~85 mm/yr [*DeMets*, 2001; *Kimura et al.*, 1997]. Generation of the oceanic lithosphere at two different spreading centers and interaction with the Galápagos hot spot results in along-strike variations in the morphology of the incoming Cocos Plate. Relatively smooth oceanic crust, originating from the East Pacific Rise, subducts northwest of the Nicoya Peninsula in Costa Rica. Further to the
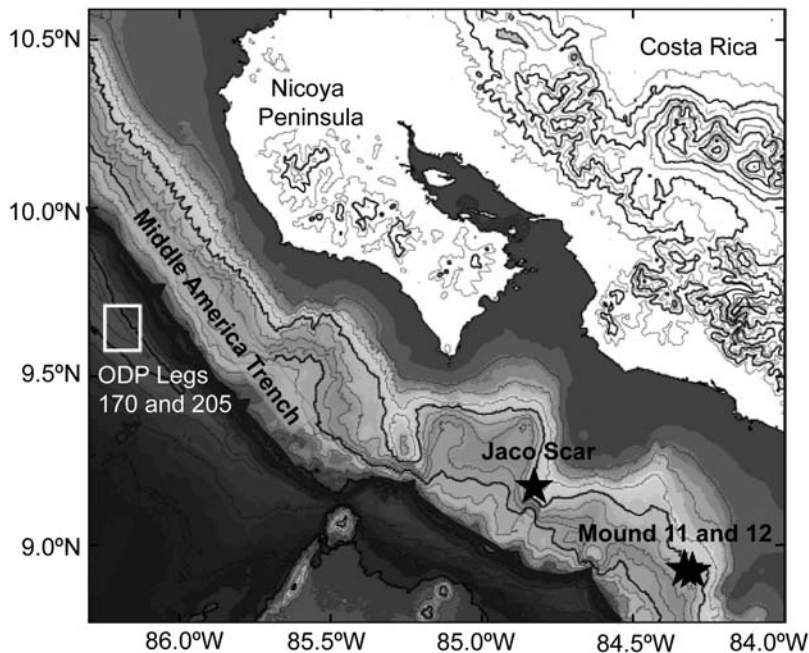
Figure 1. Regional map of the Costa Rica segment of the Central America convergent margin showing the locations of Mound 11, Mound 12, and Jaco Scar at the outer fore arc, as well as ODP legs 170 and 205 [*Kimura et al.*, 1997].

southeast, the incoming plate, generated at the Cocos-Nazca spreading center, exhibits a rough surface with numerous seamounts [*von Huene et al.*, 2000]. The subduction of seamounts causes severe deformation and subduction erosion of the overriding plate [*Fisher et al.*, 1998; *Ranero and von Huene*, 2000; *von Huene et al.*, 2000]. Mass removal from the upper plate results in subsidence, extension and formation of normal faults, which may act as pathways for ascending fluids [*McIntosh and Silver*, 1996; *Ranero and von Huene*, 2000].

[6] The incoming sedimentary section of the Cocos Plate is relatively thin (~380 m). It can be divided into three units: the uppermost unit is composed of diatomaceous ooze with ash and sand layers, the underlying unit consists of silty clay with ash layers, and the lowermost unit comprises calcareous and siliceous ooze [*Kimura et al.*, 1997]. Results obtained during Ocean Drilling Program (ODP) Leg 170 revealed that nearly the entire column of incoming sediments is underthrust beneath the toe of the Caribbean Plate without frontal offscraping or sediment accretion, indicating that the Costa Rica margin is either nonaccretionary or that underplating may be taking place further landward [*Kimura et al.*, 1997; *Vannucchi and Tobin*, 2000]. Underthrusting leads to rapid compaction of the upper hemipelagic sediments and dewatering of pore water within the first few kilometers of subduction [*Shipley and Moore*, 1986; *Shipley et al.*, 1990; *McIntosh and*

Sen, 2000; *Saffer et al.*, 2000; *Saito and Goldberg*, 2001; *Spinelli and Underwood*, 2004]. In addition to mechanically induced shallow dewatering near the toe of the overriding plate, deep-sourced fluids are released by mineral dehydration reactions and phase transformations at depths of ~10 to 15 km (between ~60°C and 140°C) [*Spinelli and Saffer*, 2004; *Spinelli and Underwood*, 2004]. While some of the deeply sourced fluids migrate along the décollement toward the deformation front [*Chan and Kastner*, 2000], most of the fluids released during dehydration reactions ascend through the overriding plate along deep-penetrating faults, producing numerous fluid venting sites on the continental slope of Costa Rica [*Ranero et al.*, 2008]. Detailed surveying of the seafloor offshore Nicaragua and Costa Rica has revealed that fluid seepage is associated with mounds (i.e., cone-shaped or slightly elongated edifices, typically ≤1 km wide and 50–100 m high), faults, seamount subduction scars, and slope failures [*Kahn et al.*, 1996; *Bohrmann et al.*, 2002; *Klaucke et al.*, 2008; *Sahling et al.*, 2008; *Ranero et al.*, 2008].

[7] In this study, we target Mound 11, Mound 12 and Jaco Scar for sampling of seep fluids for their dissolved volatile characteristics. The three sampling sites are located southeast of the Nicoya Peninsula, ~30 km arcward from the Middle America Trench (Figure 1). Jaco Scar is an 8 km wide erosive structure formed by the subduction of a seamount

[*Huehnerbach et al.*, 2005]. The landslide headwall consists of two distinct scarps at water depths between 800 and 1900 m [*Bohrmann et al.*, 2002]. Mound 11 and Mound 12 are two mud volcanoes located at 1000 m water depth. Mound 12 has a cone-shaped summit several hundred meters in diameter that rises ~50 m above the seafloor, whereas Mound 11 is significantly smaller with two distinct summits that are about 15 m (11a) and 25 m (11b) high [*Tryon et al.*, 2006, 2010].

[8] The seep sites at Mound 11, Mound 12 and Jaco Scar are characterized by the presence of authigenic carbonates and chemosynthetic communities (e.g., bacterial mats, vesicomyid clams, and/or tubeworm colonies) on the seafloor, as well as elevated methane concentrations in the water column [*Bohrmann et al.*, 2002; *Schmidt et al.*, 2005; *Mau et al.*, 2006, 2007] and high concentrations of dissolved methane and sulfide in sediment pore waters [*Hensen et al.*, 2004; *Linke et al.*, 2005]. Uniquely, gas hydrates and methane of a primarily thermogenic origin were recovered at Mound 11 [*Schmidt et al.*, 2005]. A deep origin of the methane-rich seep fluids emanating at Mound 11 was also proposed by *Hensen et al.* [2004] on the basis of the observed chlorinity depletion and boron enrichment, combined with the $\delta^{18}O$ and δD isotope composition of the fluids. The chemistry was interpreted to reflect fluid formation by clay-mineral dehydration within the subducted sediments and subsequent fluid ascent through the upper plate along deep-seated faults from ≥12 km depth, i.e., from a source depth near the updip limit of the seismogenic zone [e.g., *Newman et al.*, 2002]. However, seep fluid sampling at Mound 11 in 2005–2006 revealed an unusually high B/Li ratio of the fluids, suggesting that the source may be a mixture of subducted sediment and eroded upper plate material [*Tryon et al.*, 2010]. Taken together, these observations indicate that Mound 11 may be one of the most active and deepest sourced fluid venting sites along the Central America convergent margin.

[9] Previous attempts to quantify fluxes of fluids and chemical species (e.g., methane) at the mounds in the outer fore-arc region were based on observed methane concentrations in the near-bottom water [*Mau et al.*, 2006] or involved geochemical modeling of measured heat fluxes and concentration profiles in pore waters [*Hensen et al.*, 2004; *Linke et al.*, 2005; *Ranero et al.*, 2008]. However, published fluid flux estimates for five of the major mound structures (Mound Culebra, Mound 10, Mound 11, Mound 12, Mound Quepos) [*Hensen et al.*, 2004; *Linke et al.*, 2005; *Mau et al.*, 2006] vary over several orders of magnitude between different sites and even at particular seep locations [*Hensen et al.*, 2004; *Mau et al.*, 2006]. In part, this study will address both spatial and temporal variations in fluid fluxes by targeting Mounds 11 and 12.

3. Sampling and Analytical Techniques

[10] Seep fluids were collected at Mound 11 and Mound 12 utilizing Chemical and Aqueous Transport (CAT) meters (see *Tryon et al.* [2001] for description) operating in continuous pumping mode. The submarine flux meters were deployed during cruise AT-11–28 in June 2005 using DSV *Alvin* operated from R/V *Atlantis*. After a period of 12 months, the instruments were retrieved from the seafloor for subsequent laboratory determination of flow rates, major ion concentrations and dissolved volatile (helium, neon and CO_2) characteristics. Additional near-bottom water samples were collected within a tubeworm field at Jaco Scar using major Ti bottles during *Alvin* Dive 4131.

[11] The CAT meter is designed to measure seep fluid flow at the seafloor by channeling fluids, sampled via a collection chamber placed over the focus of the seep, through the instrument. Plastic sampling coils preserve a serial record of major ion concentrations and seep fluid flow rates (inferred from the degree of dilution of a chemical tracer), whereas 1/8 inch diameter copper coils capture fluids for determination of dissolved volatile characteristics over the duration of the deployment (see *Füri et al.* [2009] for details on sampling procedures). We note that volatile anomalies are not significantly attenuated by diffusion or dispersion in the copper tubing, as discussed by *Barry et al.* [2009]. The characteristic diffusion length (x) for helium in fresh water at 5°C is ~40 cm for a 12 month deployment (x = $\sqrt{Dt}$ where D = 5.1×10^{-5} cm²/s [*Jähne et al.*, 1987] and t = time). Thus, the helium signal may be slightly impacted, and aliquots collected early during a deployment will experience greater diffusive smearing of a helium pulse compared to later samples. Dispersion of the signal is a potentially greater problem, with differential flow between water close to the tubing wall versus that in the center of the tube acting to smear out sharp concentration gradients. However, diffusion tends to counter this effect in small diameter tubes at low flow rates [*Cussler*, 1984]. Furthermore, *Tryon et al.* [2001] found that dispersion and diffusion were insignificant during a 70 day submarine tracer test using 2.4 mm diameter tubing at a flow rate of ~1 m/d.

Table 1. Chemical Content of Seep Fluids From Mound 11a and Mound 12, as Well as Seawater Values[a]

	R29	S28	I22	Seawater
Cl (mM)	397	554	551	546
Ca (mM)	6.0	10.2	10.3	10.3
K (mM)	7.1	10.4	10.5	10.2
Mg (mM)	30	53	53	53
Na (mM)	322	478	473	470
B (μM)	881	397	422	416
Li (μM)	18.1	25.6	25.4	25.2
Sr (μM)	44.6	86.5	80.5	90.2

[a]Fluids from Mound 11a were sampled using CAT meter R29, fluids from Mound 12 were sampled using CAT meters S28 and I22, and seawater values are from IAPSO standard [*Tryon et al.*, 2006, 2010].

[12] Following instrumentation recovery, the copper tubing was sectioned to produce a quasi-continuous temporal record of the dissolved volatile content. Based on the duration of the deployment and the location of the interface between the saline seep fluid and the deionized water which initially filled the coils, we calculated a fluid sampling rate of ~0.9 ml/d. Thus, each section of analyzed copper coil represents a specific time interval, with 0.4 m of coil corresponding to ~1 day of fluid sampling.

[13] Copper coils were cut and sealed into sections of ~0.4 m length using refrigeration clamps, and attached to an ultrahigh vacuum system for sample extraction and processing [see *Kulongoski and Hilton*, 2002; *Füri et al.*, 2009]. The extraction system was interfaced directly to the noble gas mass spectrometer preparation line, so that the total helium and neon load released from the Cu coils was transferred to the MAP 215 noble gas mass spectrometer. Helium and neon abundances as well as the ^{3}He/^{4}He ratios were determined for a subset of seep fluid samples. Sample ^{3}He/^{4}He ratios and ^{4}He/^{20}Ne ratios were calibrated against air standards of known amount run under identical experimental conditions.

[14] All fluid samples were acidified to ensure release of the total CO_2; consequently, CO_2 amounts represent the total dissolved inorganic carbon content. The CO_2 fraction of each sample was collected during the extraction procedure by freezing into a Pyrex break seal for transfer to a dedicated purification and measurement system. A variable temperature trap was used to separate CO_2 from any other species after which the $\sum CO_2$ abundances were measured manometrically in a calibrated volume. The $\delta^{13}C_{\sum CO_2}$ values, reported relative to the international reference standard Vienna Pee Dee Belemnite (VPDB), were measured from an

aliquot of this gas using a VG Prism stable isotope mass spectrometer or a Delta V Isotope Ratio mass spectrometer.

4. Results

[15] Following instrumentation recovery, the first step was determination of flow rates and major ion concentrations in the plastic sampling coils in order to identify which flux meters had recorded active seep fluid venting. In Table 1, we show the chemical composition of seep fluids collected at mounds 11 and 12. Fluids sampled at Mound 11a (CAT R29) show a low salinity and altered fluid chemistry with elevated B and low Ca, K, Mg, Na, Li and Sr concentrations relative to seawater. Flow rates were 2–5 cm/yr through most of the 12 month record. However, increased flow rates were measured near the beginning and end of our record, as well as in mid-October 2005 (Figures 3e and 3f). At Mound 12, coil S28 recorded highly variable flow rates; however, the chemistry of the sampled fluids is similar to seawater throughout the deployment. The sampling chamber connected to coil I22, also from Mound 12, was accidentally flipped over on 9 October 2005 during ROV operations on the site. Thus, after this date, CAT meter I22 sampled ambient bottom seawater, and the fluids are expected to have a seawater-like volatile content.

[16] Since only CAT meter R29, deployed at Mound 11a, sampled fluids with chemistry altered from seawater values, we targeted this particular sampling coil for detailed volatile analyses in order to resolve any temporal variations of the dissolved CO_2 content of the captured fluids (section 5.2).

4.1. Helium and Neon Abundances

[17] Helium and neon results for a subset of submarine seep fluids collected at Mound 11a, Mound 12, and Jaco Scar are reported in Table 2. Results are shown as measured ^{4}He and ^{20}Ne concentrations ([^{4}He]$_m$ and [^{20}Ne]$_m$).

[18] Measured helium concentrations ([^{4}He]$_m$) of seep fluids collected at mounds 11a and 12 range from 47.8 to 54.3 ncm^3 STP/g H$_2$O, whereas the neon concentrations vary between 179.5 and 228.7 ncm^3 STP/g H$_2$O (Table 2). The helium and neon abundances are slightly higher than expected values for ambient air-saturated seawater (i.e., [^{4}He]$_{SW}$ = 40.3 ncm^3 STP/g H$_2$O and [^{20}Ne]$_{SW}$ = 158.8 ncm^3 STP/g H$_2$O at 5°C [*Weiss*, 1971]), even for sample I22-1, which was collected after the sampling chamber had been decoupled from the seafloor.

Table 2. Helium and Neon Systematics of Submarine Seep Fluids, Costa Rica[a]

Sample ID	^{3}He/^{4}He (R_m/R_A)	$[^4$He$]_m$ (ncm^3 STP/g H$_2$O)	$[^{20}$Ne$]_m$ (ncm^3 STP/g H$_2$O)	^{4}He/^{20}Ne
	Mound 11a: CAT Meter R29			
R29-1	1.34 ± 0.03	47.9 ± 6.0	179.5 ± 18.3	0.27
R29-2	1.21 ± 0.03	47.8 ± 5.8	199.7 ± 20.3	0.24
R29-3	1.22 ± 0.03	52.8 ± 6.4	216.9 ± 22.0	0.24
R29-4	1.22 ± 0.03	54.3 ± 6.5	228.7 ± 23.2	0.24
R29-5	1.04 ± 0.02	49.7 ± 3.4	197.2 ± 20.1	0.25
	Mound 12: CAT Meter S28			
S28-1	1.24 ± 0.03	50.1 ± 6.0	222.8 ± 22.6	0.23
	Mound 12: CAT Meter I22			
I22-1	1.06 ± 0.03	50.5 ± 6.2	206.0 ± 20.9	0.25
	Jaco Scar: Alvin Dive 4131			
Alvin major bottle	1.31 ± 0.03	84.4 ± 0.9	114.0 ± 1.2	0.74
Alvin major bottle	1.23 ± 0.06	86.7 ± 0.9	115.5 ± 1.2	0.75
Seawater (5°C)	1	40.3[b]	158.8[b]	0.25

[a]All errors are reported at the 1 σ level. The smaller errors for $[^4$He$]_m$ and $[^{20}$Ne$]_m$ for the samples from Jaco Scar are due to the larger amounts of fluids processed and the correspondingly lower uncertainty on the measured gas concentrations.

[b]Amount of gas absorbed per volume of seawater, assuming an air equilibration temperature of 5°C. Note that the solubilities do not change significantly with temperature, e.g., $[^4$He$]_{eq}$ = 39.3 ncm^3 STP/g H$_2$O at 15°C.

Near-bottom water samples from Jaco Scar, on the other hand, are significantly oversaturated in helium ($[^4$He$]_m \approx 85$ ncm^3 STP/g H$_2$O) and depleted in neon ($[^{20}$Ne$]_m \approx 115$ ncm^3 STP/g H$_2$O) relative to air-equilibrated seawater. Thus, these fluids show elevated ^{4}He/^{20}Ne ratios compared to ambient seawater, while the ^{4}He/^{20}Ne ratios of samples from the mounds are similar to or slightly lower than seawater values.

4.2. Ratios of ^{3}He/^{4}He

[19] Measured helium isotope ratios are reported in Table 2 as R_m/R_A, where R_m = ^{3}He/^{4}He ratio measured in the sample and R_A = ^{3}He/^{4}He ratio of air = 1.4 × 10^{-6}.

[20] The ^{3}He/^{4}He ratios range from 1.04 to 1.34 R_A and appear significantly higher that the isotope composition of helium produced in crustal lithologies by radioactive decay (~0.05 R_A [*Andrews*, 1985]). Measured helium isotope ratios in water samples are usually corrected for the presence of atmosphere-derived helium, from air directly or water. By monitoring the sample He/Ne ratio and, assuming all the neon is derived from air or air-equilibrated water, the atmospheric helium component can be subtracted from the sample helium utilizing the known He/Ne ratio of air or air-saturated water, respectively [*Hilton*, 1996]. However, noble gas concentrations in pore fluids and seawater at submarine cold seep sites can be affected by the presence of methane gas bubbles [*Brennwald*

et al., 2003; *Han et al.*, 2004; *Brennwald et al.*, 2005; *Schmidt et al.*, 2005; *Holzner et al.*, 2008; *Füri et al.*, 2009]. Gas exchange between the bubbles and the surrounding pore water in the sediment column can potentially strip dissolved gases from the fluid phase until either the gas bubbles escape or until equilibrium is established between gas concentrations in the bubbles and the surrounding fluid. Thus, stripping can decrease noble gas concentrations in pore fluids, and it can also lead to fractionation of noble gas elemental patterns, due to the systematic increase in water solubility and decrease in diffusion coefficients of the noble gases with increasing atomic mass [*Ballentine et al.*, 2002; *Leifer and Clark*, 2002; *Brennwald et al.*, 2003, 2005; *Holzner et al.*, 2008]. Bubbles preferentially strip helium due to its low solubility and/or high diffusivity, thereby decreasing the He/Ne ratio in the residual pore water. As escaping methane bubbles dissolve in the water column, however, helium is expected to be transferred to the bottom water at an early stage because it diffuses much faster out of the bubbles than neon.

[21] We suggest that the neon depletion in near-bottom water samples collected at Jaco Scar indicates that seep fluids emanating at the Costa Rica margin have lost a fraction of their dissolved noble gases by interaction with methane bubbles. The helium enrichment, on the other hand, may be caused by noble gas dissolution from rising methane bubbles and/or addition of a terrigenic (i.e., crustal and/or mantle-derived) helium com-

Table 3. Carbon Systematics of Submarine Seep Fluids, Costa Rica

Sample ID	Section in Coil (m From Inlet)	Time Elapsed After Deployment (Days)	$[\sum CO_2]$ (cm³ STP/g H₂O)	$\delta^{13}C_{\sum CO2}$ (‰ VPDB)
		Mound 11a: CAT Meter R29		
R29-1	136.75–137.16	30 (10 Jul 2005)	0.17 ± 0.02	−12.62 ± 0.02
R29-2	106.17–106.58	106 (24 Sep 2005)	0.31 ± 0.03	−11.46 ± 0.02
R29-6	105.76–106.17	107 (25 Sep 2005)	0.28 ± 0.03	−14.67 ± 0.02
R29-7	105.36–105.76	108 (26 Sep 2005)	0.18 ± 0.02	−23.90 ± 0.03
R29-8	104.95–105.36	109 (27 Sep 2005)	0.21 ± 0.02	−23.39 ± 0.02
R29-9	103.73–104.95	110 (28 Sep 2005)	0.34 ± 0.03	−11.60 ± 0.02
R29-10	102.51–103.73	113 (1 Oct 2005)	0.17 ± 0.02	−20.66 ± 0.03
R29-11	101.29–102.51	116 (4 Oct 2005)	0.32 ± 0.03	−14.72 ± 0.02
R29-12	100.07–101.29	119 (7 Oct 2005)	0.15 ± 0.02	−20.41 ± 0.04
R29-13	98.85–100.07	122 (10 Oct 2005)	0.16 ± 0.02	−21.47 ± 0.02
R29-14	97.64–98.85	125 (13 Oct 2005)	0.17 ± 0.02	−22.61 ± 0.04
R29-15	96.42–97.64	128 (16 Oct 2005)	0.15 ± 0.02	−21.24 ± 0.04
R29-16	95.20–96.42	131 (19 Oct 2005)	0.15 ± 0.02	−21.75 ± 0.05
R29-3	75.72–76.12	182 (9 Dec 2005)	0.33 ± 0.03	−15.47 ± 0.01
R29-4	45.38–45.78	258 (21 Feb 2006)	0.34 ± 0.03	−14.49 ± 0.02
R29-5	0–0.41	371 (15 Jun 2006)	0.16 ± 0.01	−22.06 ± 0.01
		Mound 12: CAT Meter S28		
S28-1	136.75–137.16	30 (10 Jul 2005)	0.14 ± 0.01	−60.35 ± 0.02
S28-2	13635–136.75	31 (11 Jul 2005)	0.18 ± 0.02	−65.02 ± 0.07
S28-3	135.94–136.35	32 (12 Jul 2005)	0.11 ± 0.01	−68.18 ± 0.03
S28-4	135.53–135.94	33 (13 Jul 2005)	0.10 ± 0.01	−66.11 ± 0.04
		Mound 12: CAT Meter I22		
I22-4	1.34–1.75	367 (11 Jun 2006)	0.007 ± 0.001	−14.65 ± 0.29[a]
I22-3	0.94–1.34	368 (12 Jun 2006)	0.011 ± 0.001	−11.83 ± 0.47[a]
I22-2	0.53–0.94	369 (13 Jun 2006)	0.019 ± 0.001	−12.96 ± 0.33[a]
I22-1	0.13–0.53	370 (14 Jun 2006)	0.016 ± 0.001	−18.03 ± 0.01
		Jaco Scar: Alvin Dive 4131		
Alvin major bottle			0.006 ± 0.001	−21.90 ± 0.01
Alvin major bottle			0.066 ± 0.007	0.68 ± 0.02
Pacific seawater			0.06[b]	~0.3[c]

[a]Values of $\delta^{13}C_{\sum CO2}$ were determined on a Delta V Isotope Ratio mass spectrometer; all other $\delta^{13}C_{\sum CO2}$ values were determined on a VG Prism stable isotope mass spectrometer.
[b]*Simpson and Broecker* [1973].
[c]*Kroopnick* [1985].

ponent. Since the noble gas elemental ratio prior to noble gas stripping for the deeply sourced seep fluids is unknown, the observed $^3He/^4He$ ratios in our samples cannot be corrected for the presence of atmosphere-derived helium. However, subtracting the atmospheric helium component from the sample helium will result in a shift to higher helium isotope ratios for samples with measured $^3He/^4He$ ratios > 1 R_A. Thus, all $^3He/^4He$ ratios which are greater than the atmospheric value represent minimum estimates for the air-corrected helium isotope composition. Therefore, these elevated ratios are consistent with a small but discernable contribution of mantle-derived helium (8 R_A [*Graham*, 2002]) to fluids emanating along the submarine section of the Costa Rica fore arc (see section 5.1.1 for discussion).

4.3. Carbon Abundances and Isotope Ratios

[22] The $\sum CO_2$ abundances (i.e., total dissolved inorganic carbon) and carbon isotope ratios are reported in Table 3 together with information on the specific sampling interval represented by each section of the analyzed coil. Thus, the sampling coils have preserved a temporal record of variations in the dissolved carbon characteristics of the captured fluids.

[23] Measured $\sum CO_2$ concentrations in the seep fluid samples range from 0.006 to 0.34 cm³ STP/g H₂O (Table 3 and Figure 2). Fluids in coils R29 and S28 are supersaturated in $\sum CO_2$ with respect to seawater (i.e., $[\sum CO_2]_{SW} \approx 0.06$ cm³ STP/g H₂O in water from the deep Pacific [*Simpson and Broecker*, 1973]), indicating addition of extraneous carbon.
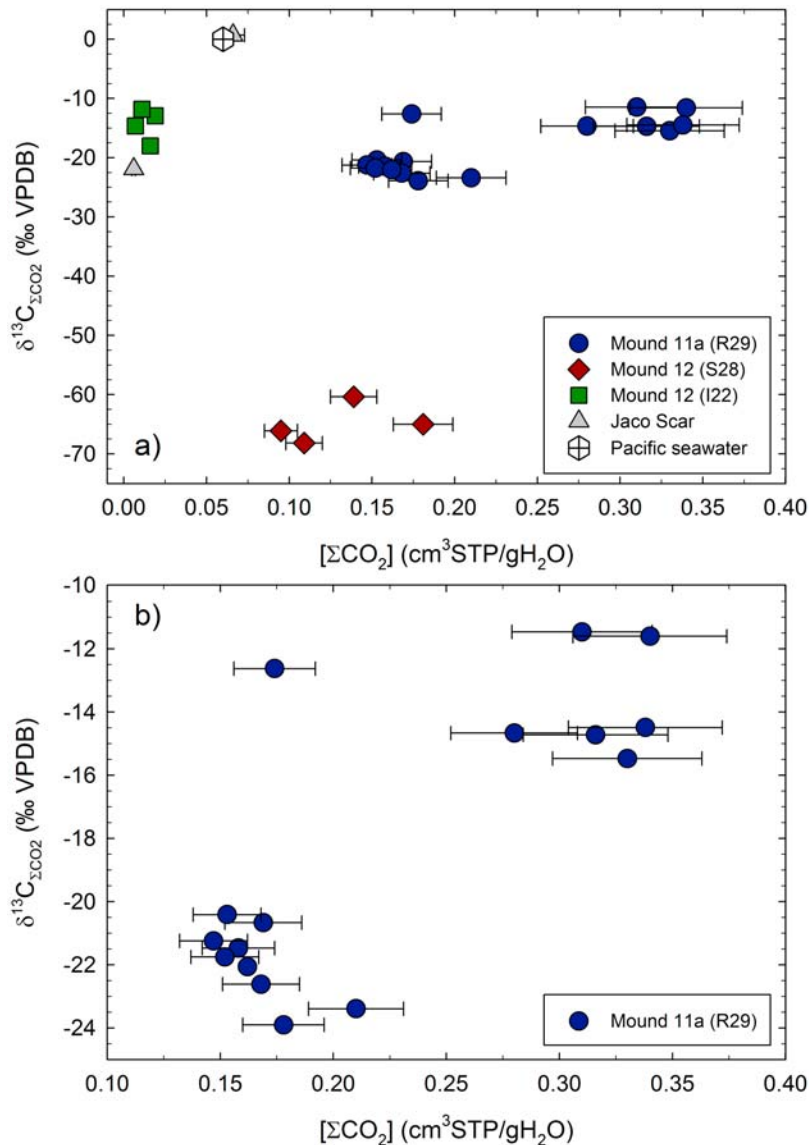
Figure 2. (a) Carbon isotope composition, $\delta^{13}C_{\Sigma CO2}$, versus measured ΣCO_2 (i.e., total dissolved inorganic carbon concentrations) for seep fluids collected at Mound 11a (CAT meter R29), Mound 12 (CAT meters S28 and I22), and Jaco Scar (*Alvin* major Ti bottles), as well as deep Pacific seawater [*Kroopnick*, 1985; *Simpson and Broecker*, 1973] and (b) expanded version showing the data for Mound 11a (CAT meter R29) only. Errors are shown at the 1σ level.

However, one near-bottom water sample collected at Jaco Scar and bottom seawater collected at Mound 12 with coil I22 appear to be undersaturated in ΣCO_2 relative to seawater. During our survey dives, we observed dense forests of vestimentiferan tubeworms and clam fields at Jaco Scar as well as extensive tubeworm colonies at Mound 12. Thus, the CO_2 depletion in the bottom seawater may results from uptake of DIC by the seep biota. The carbon isotope composition of one fluid sample collected at Jaco Scar is similar to ambient seawater (i.e., $\delta^{13}C_{\Sigma CO2} \approx 0.3‰$ [*Kroopnick*, 1985]), whereas the $\delta^{13}C_{\Sigma CO2}$ values of all other seep fluids samples

range from −11‰ to −68‰. However, we note that extremely low $\delta^{13}C_{\Sigma CO2}$ values (<−60‰) are only observed in one sampling coil at Mound 12 (i.e., CAT meter S28).

5. Discussion

[24] Our survey of submarine seep fluids demonstrates that the volatile chemistry of fluids emanating at the Costa Rica margin shows significant spatial and temporal variability. In the following sections, we (1) evaluate the origin of dissolved volatiles in

the seep fluids and (2) attempt to quantify the fore-arc carbon output through submarine fluid venting.

5.1. Origin of Dissolved Volatiles

5.1.1. Mantle Helium Release at the Costa Rica Fore Arc

[25] Helium isotopes are a powerful tool to recognize mantle-crust interactions in a variety of geotectonic settings. The rare isotope (^{3}He) is essentially primordial and retained in the Earth's interior whereas ^{4}He is continuously produced by the decay of U and Th. Thus, any ^{3}He/^{4}He ratio in terrestrial fluids greater than the local crustal production rates (i.e., ratios significantly greater than values of ~0.05 R_A [*Andrews*, 1985]) indicates the presence of mantle-derived helium.

[26] Seep fluids collected at Mound 11, Mound 12, and Jaco Scar show minimum helium isotope ratios of 1.3 R_A (see section 4.2), suggesting that mantle-derived helium is released by submarine fluid venting at the Costa Rica fore arc. Furthermore, groundwaters collected on the Nicoya Peninsula and the adjacent coast also show ^{3}He/^{4}He ratios between 0.45 and 3 R_A, which equates to a mantle contribution up to ~38% of the total He in these fluids [*Hilton et al.*, 2009]. Magmatic activity can be ruled out as the source of mantle helium in this region. Notably, however, high ^{3}He/^{4}He ratios (i.e., greater than crustal production rates) have previously been reported for other fore-arc regions, such as SW Japan [*Matsumoto et al.*, 2003; *Dogan et al.*, 2006; *Umeda et al.*, 2006, 2007], New Zealand [*Giggenbach et al.*, 1993], the Nankai Trough [*Kastner et al.*, 1993], the Cook Inlet of Alaska [*Poreda et al.*, 1988], and the Solomon Islands [*Trull et al.*, 1990]. In fore-arc regions, slab-derived fluids may acquire mantle helium during their ascent through the serpentinized mantle wedge. While seismic velocities along the Nicoya Peninsula are consistent with the presence of a serpentinized fore-arc mantle wedge in Costa Rica, the continental Moho intersects the downgoing oceanic slab ~100 km arcward from the trench at a depth of 30–34 km [*DeShon and Schwartz*, 2004]. Mound 11, Mound 12 and Jaco Scar are located significantly closer to the trench and thus, a mantle wedge is not present beneath the sampled seep locations. However, it has previously been suggested that the Costa Rica margin contains several oceanic igneous basement complexes, formed from a primitive mantle source [*Sinton et al.*, 1997; *Kerr et al.*, 1998; *Hauff et al.*, 2000a]. The Nicoya Complex marks the westernmost edge of the Caribbean Large Igneous

Province (CLIP), an oceanic plateau produced by massive volcanism over the Galápagos hot spot. It formed between 95 and 83 Ma and consists of tholeiitic volcanics (pillow lavas and massive sheet flows), locally intruded by gabbros and plagio-granites [*Hauff et al.*, 2000a; *Sinton et al.*, 1997]. In addition, lavas described as komatiites have been located on the Nicoya Peninsula [*Alvarado et al.*, 1997]. In contrast, the Quepos Complex (65–59 Ma [*Hauff et al.*, 2000a]), further to the southeast, is thought to represent an accreted seamount of the early Galápagos hot spot track [*Sinton et al.*, 1997]. Olivine separates of two enriched picrites collected at Quepos show high ^{3}He/^{4}He ratios of ~12 R_A, consistent with a helium contribution from the Galápagos hot spot [*Hauff et al.*, 2000b]. Thus, if the fore-arc basement rocks in Costa Rica can be linked to the Galápagos hot spot or the CLIP, fluids derived from compaction and/or dehydration of subducting slab sediments and eroded fore-arc material may acquire a high-^{3}He signature during serpentinization within the subduction channel and upper plate.

[27] Alternatively, *Umeda et al.* [2006] proposed that aqueous fluids generated by dehydration of the downgoing slab may entrain helium derived from the mantle lithosphere portion of the downgoing plate. As the fluids migrate to the surface, the original ^{3}He/^{4}He ratio is lowered by addition of radiogenic ^{4}He from the crust and/or mixing with shallow fluids. Thus, mantle helium released through submarine fluid venting at the Costa Rica fore arc possibly originates from the lithospheric mantle of the Cocos Plate. *Kennedy et al.* [1997] and *Kennedy and van Soest* [2007] showed that crustal faulting plays an important role in the transfer of mantle-derived helium through the crust. In this case, normal faults within the toe of the Caribbean Plate would represent the permeable conduits that allow mantle fluids to leak through the crust and impart elevated ^{3}He/^{4}He ratios to the seep fluids emanating at Mound 11, Mound 12 and Jaco Scar. We note that assessing the helium provenance for fluids released along the Costa Rica fore arc is the topic of continuing studies [e.g., *Hilton et al.*, 2009] and is beyond the scope of this contribution.

5.1.2. Dissolved Inorganic Carbon in Costa Rica Seep Fluids

[28] The DIC content of seep fluids emanating at the Costa Rica fore arc may be derived from a number of potential sources. These include (1) seawater, (2) methanogenesis, (3) in situ oxidation of

marine organic matter, (4) anaerobic methane oxidation, (5) precipitation/dissolution of authigenic carbonates, and/or (6) the mantle. The isotope composition of the DIC can, in principle, be used to distinguish between these possibilities and identify its origin. However, interplay of various processes and mixing of DIC derived from several sources severely impedes a definitive assessment of the origin of DIC in the seep fluids sampled at Mound 11, Mound 12, and Jaco Scar.

[29] The carbon isotope composition, $\delta^{13}C_{\sum CO2}$, of the collected seep fluids is significantly lower than that of eastern Pacific seawater (~0.3‰ at 1 km depth [Kroopnick, 1985]), except for one near-bottom water sample collected at Jaco Scar. Consequently, ocean bottom water can be ruled out as the dominant source of DIC in the fluids sampled at mounds 11 and 12.

[30] Methanogenesis by bacterial CO_2 reduction below the sulfate reduction zone,

$$CO_2 + 4H_2 \rightarrow CH_4 + H_2O, \qquad (1)$$
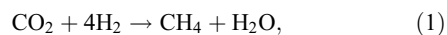
probably represents the principal mechanism for biogenic methane formation in marine sediments [Whiticar and Faber, 1986]. Methanogenesis produces isotopically depleted methane ($\delta^{13}C_{CH4}$ = −110‰ to −50‰) and a ^{13}C-enriched DIC pool due to a fractionation effect of about 60‰ [Whiticar, 1999]. At the Costa Rica fore arc, methane and residual DIC are likely carried from depth to the surface at cold seep sites by upward flow of fluids derived from sediments of the subducting slab [Hensen et al., 2004]. Indeed, previous work has shown that DIC in pore waters at Mound 11 has an isotopic signature of methanogenesis, with $\delta^{13}C_{DIC}$ values up to +20‰ [Han et al., 2004]. However, the $\delta^{13}C_{\sum CO2}$ values observed in our study at mounds 11 and 12 are significantly lower, i.e., between −11‰ and −68‰, suggesting that a significant fraction of DIC in our samples is derived from oxidation of ascending isotopically depleted methane.

[31] One of the main biogeochemical processes within the sediments at cold seep sites is the microbially mediated anaerobic oxidation of methane via sulfate reduction according to the reaction [Boetius et al., 2000]:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O. \qquad (2)$$
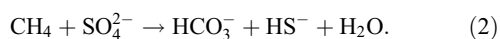
Thus, when fluid flow rates are low, the ascending dissolved methane is completely oxidized by this process, which generates DIC with a $\delta^{13}C$ range reflecting mainly the isotope composition of oxidized methane. At Mound 11, bottom water methane has a carbon isotope ratio of ~−45‰, whereas $\delta^{13}C_{CH4}$ values at Mound 12 are about 30‰ lower ($\delta^{13}C_{CH4} \approx -75$‰), indicating a deep (thermogenic) source of methane, i.e., methane generation by degradation of organic matter within the subducted slab [Han et al., 2004; Schmidt et al., 2005]. Therefore, $\delta^{13}C_{\sum CO2}$ values between −68‰ and −60‰ in seep fluids collected at Mound 12 appear consistent with a significant contribution of carbon derived from oxidation of biogenic methane.

[32] Aside from anaerobic methane oxidation, microbial oxidation of marine organic matter can produce ^{13}C-depleted DIC in the pore waters of deep-sea sediments. Above and within the zone of sulfate reduction, oxidation of sedimentary organic matter produces DIC that inherits the low $\delta^{13}C$ values of the organic carbon (−20‰ to −25‰), assuming little or no fractionation during organic matter oxidation:

$$CH_2O + SO_4^{2-} \rightarrow \sum CO_2 + S^{2-} + 2H_2O, \qquad (3)$$
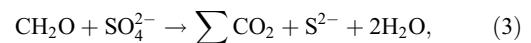
where CH_2O represents organic matter. While organic matter degradation likely represents an important source of DIC for the sampled seep fluids, $\delta^{13}C_{\sum CO2}$ values at Mound 12 are significantly lower than is possible if the DIC originates from oxidation of sedimentary organic matter alone.

[33] We note that extensive carbonate crusts and large carbonate rocks were observed during our survey of Mound 12, whereas Mound 11a showed less extensive carbonate cover. Precipitation of authigenic carbonate may remove a significant fraction of DIC; however, this process has a negligible effect on the isotope composition of the dissolved carbon phases [Emrich and Vogel, 1970]. Dissolution of carbonate minerals, on the other hand, has a variable influence on the carbon isotope composition of the DIC in bottom waters, depending on the $\delta^{13}C$ value of the carbonate that is being dissolved.

[34] Our study shows that the DIC characteristics of seep fluids emanating at the Costa Rica margin show significant spatial variability. At Mound 11, both the DIC concentrations and the $\delta^{13}C_{\sum CO2}$ values of the fluids collected in coil R29 are much higher than in coil S28 at Mound 12 (Table 3 and Figure 2). Furthermore, pore fluids sampled at Mound 11 show alkalinities of ~5 mM, whereas significantly higher alkalinities between 30 and 40 mM were measured at Mound 12 [Tryon et al., 2010]. Given that the two mounds are just 1 km

apart, fluids are expected to be derived from the same source. We suggest that at both mounds, isotopically depleted methane and ^{13}C-enriched DIC produced by deep methanogenesis are carried from depth to the surface by upward flow of fluids derived from sediments of the subducting slab. Since Mound 12 is older and is becoming less active, most of the ascending dissolved methane is likely oxidized via sulfate reduction, generating DIC with $\delta^{13}C_{\sum CO2}$ values between −68‰ and −60‰ at this site. Furthermore, anaerobic methane oxidation increases the alkalinity and leads to the precipitation of authigenic carbonates. In contrast, Mound 11 is young and more active, and fluids were sampled on a relatively fresh mudflow. Thus, the higher $\delta^{13}C_{\sum CO2}$ values are consistent with a large contribution of DIC originating from deep methanogenesis (with $\delta^{13}C_{DIC}$ values up to +20‰ [*Han et al.*, 2004]; see above), only slightly diluted by DIC derived from anaerobic oxidation of methane and/or oxidation of marine organic matter. In addition, high helium isotope values in fluids collected at Mound 11 and Mound 12 as well as Jaco Scar (see section 4.2) are consistent with a small contribution of mantle-derived volatiles. Thus, a fraction of the dissolved carbon likely originates from the mantle ($\delta^{13}C \approx -6.5$‰ [*Marty and Jambon*, 1987]).

5.2. Temporal Variations of the Dissolved Carbon Content

[35] Time series studies at a number of locations have revealed that gas and fluid emission at cold seep sites is not a continuous process but exhibits strong variability at different time scales [*Tryon et al.*, 1999, 2002; *Leifer et al.*, 2004; *LaBonte et al.*, 2007; *Solomon et al.*, 2008; *Füri et al.*, 2009]. To date, little is known about the causes of these variations. Correlations between seep fluid flow rates and tides have been observed at a number of seep sites [*Tryon and Brown*, 2001; *Tryon et al.*, 2001; *LaBonte et al.*, 2007]. In contrast, *Füri et al.* [2009] proposed that a transient pulse in the flow rate at Extrovert Cliff (Monterey Bay) results from the release of mantle-derived fluids caused by fault rupturing. In addition, *Solomon et al.* [2008] and *Tryon et al.* [1999; 2002] suggested that seep flow rates can be significantly affected by localized changes in sediment permeability as a result of gas hydrate and carbonate precipitation, as well as the presence of free gas in the sediment pore space. As discussed above, we observed extensive carbonate crusts at the summit of Mound 12 during our survey dives in 2005 and 2006, whereas *Mau et al.* [2006] noted little carbonate precipitation during

previous seafloor surveys. Furthermore, episodic free gas expulsions were observed at mounds 11 and 12 in spring 2009 (L. Levin, personal communication, 2009). These observations show that fluid and gas emissions at the Costa Rica fore arc are highly variable over time.

[36] Our new carbon isotope and abundance results and related flow rate data for fluids emanating at Mound 11a show that the carbon chemistry of seep fluids fluctuates remarkably over time. Figure 3 shows the variation of the DIC characteristics of fluids collected at Mound 11a (CAT meter R29) as well as the flow rate over the 12 month deployment period. The temporal record reveals that both the DIC concentration (Figures 3a and 3b) and the isotope composition (Figures 3c and 3d) of the fluids vary over time. For most samples, low DIC abundances correlate with low $\delta^{13}C_{\sum CO2}$ values (Figures 2b and 3). We note that the carbon characteristics appear to be controlled by the fluid flow rate (Figures 3e and 3f); increased flow rates near the beginning and end of our record, as well as in mid-October 2005, result in decreased DIC concentrations. However, detailed analyses from 24 September to 19 October (Table 3 and Figure 3) reveal that the carbon flux appears to be perturbed before the onset of the spike in flow rates.

[37] Previous studies have shown that the efficiency of methane oxidation at cold seep sites depends on the rate of upward fluid flow. At high flow velocities (>100 cm/yr), the ascending fluids push the zone of anaerobic methane oxidation to shallow sediment depths or even through the sediment-water interface, so that a significant methane fraction can be expelled into bottom water [*Luff and Wallmann*, 2003]. In this case, due to the lower alkalinity production, supersaturation with respect to carbonates is diminished so that carbonate precipitation is not as extensive.

[38] Low DIC concentrations at high flow rates observed in our temporal record obtained at Mound 11a appear consistent with decreased methane oxidation. Since only a small fraction of methane is oxidized under these conditions, the $\sum CO_2$ pool is expected to become enriched in ^{12}C (i.e., yielding lower $\delta^{13}C_{\sum CO2}$ values) as the light carbon isotope is preferentially utilized during methane oxidation. Alternatively, low DIC abundances and correspondingly low $\delta^{13}C_{\sum CO2}$ values may indicate that less ^{13}C-enriched DIC is supplied from methanogenesis within the subducted sediments.

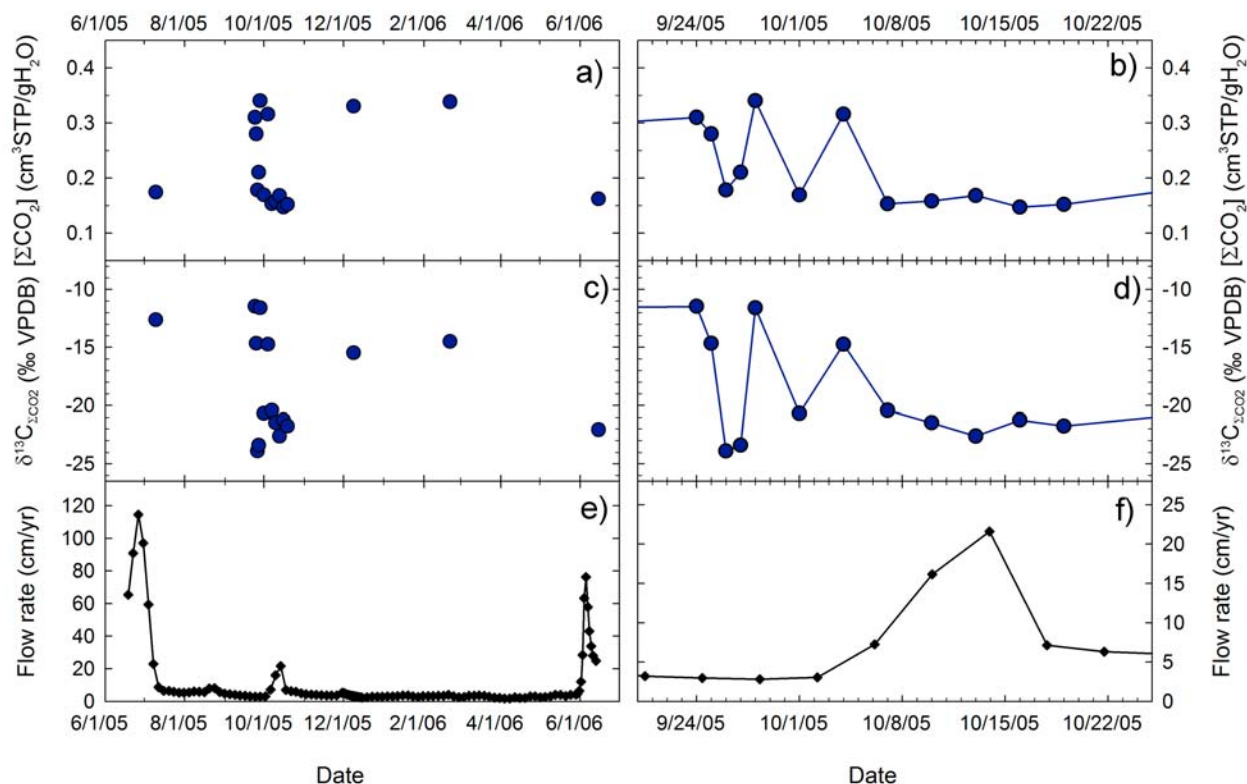**Figure 3.** Variation of (a and b) the measured $\sum CO_2$ concentration, (c and d) the carbon isotope composition, $\delta^{13}C_{\sum CO2}$, and (e and f) the flow rate for seep fluids collected at Mound 11a with CAT meter R29 over the 12 month deployment period (Figures 3a, 3c, and 3e) and during the high flow rate event in mid-October 2005 (Figures 3b, 3d, and 3f).

5.3. Mass Balance Calculations and Implications for the Carbon Flux at the Costa Rica Fore Arc

[39] The input flux of sedimentary carbon into the Costa Rica subduction zone can be estimated from (1) the masses and lithologies of the incoming sediment pile on the Cocos Plate, (2) the total carbon concentration (sedimentary organic carbon and marine carbonates) of the subducting lithologies, and (3) present-day subduction rates. *Li and Bebout* [2005] characterized the carbon concentration and isotope composition of sediments recovered offshore of Costa Rica during ODP Leg 170. By integrating the carbon content of the ~380 m thick sediment section, the total sedimentary carbon input to the Costa Rica margin is estimated at 1.6×10^9 g C km^{-1} yr^{-1}. However, subducting oceanic crust may also represent a significant input flux of carbon since carbonate veining and/or calcite precipitation associated with hydrothermal alteration affect the upper oceanic crust progressively with age [*Alt and Teagle*, 1999].

[40] A fraction of the subducted carbon will be returned to the surface by magmatism at the vol-

canic front. The CO_2 output flux for the 310 km long volcanic front in Costa Rica can be derived from SO_2 flux measurements (= 1.1×10^9 mol/yr [*Zimmer et al.*, 2004]) and observed average CO_2/SO_2 molar ratios at volcanic arcs worldwide (= 5 [*Hilton et al.*, 2002]). This flux is estimated at 2.1×10^8 g C km^{-1} yr^{-1}. However, the carbon released via the front may originate, in part, from the mantle wedge (M), as well as from slab-derived marine limestone (L) and sedimentary organic carbon (S), and possibly subducting oceanic crust. *Hilton et al.* [2002] and *Shaw et al.* [2003] assessed the carbon provenance for geothermal fluids collected along the Costa Rica volcanic front using the three end-member (M-L-S) model of *Sano and Marty* [1995], and concluded that 6%–10% of the carbon output is derived from the mantle wedge (see *Hilton et al.* [2002] for details). Thus, the volcanic front carbon flux derived from the subducted slab (i.e., marine carbonates and sedimentary organic carbon) is equal to ~1.9×10^8 g C km^{-1} yr^{-1} (Figure 4). In other words, the output flux via the front is only ~12% of the total carbon which is potentially available by sediment input via the trench. In a more recent analysis, *de Leeuw et al.*
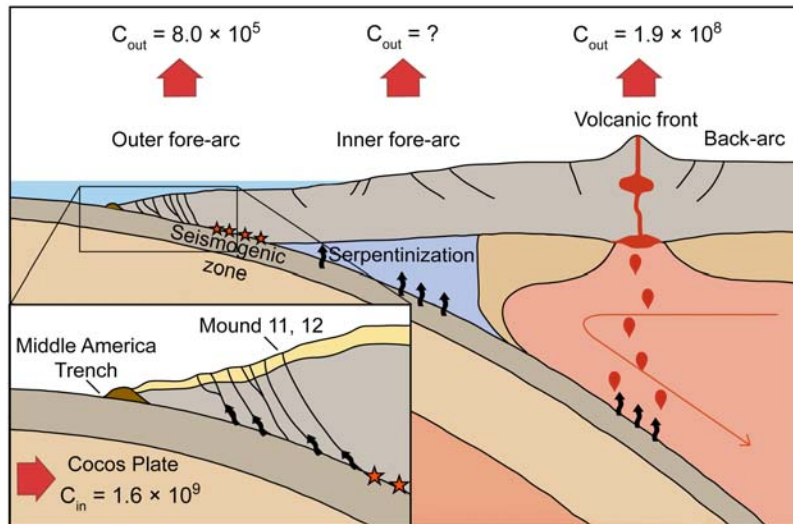
Figure 4. Simplified cartoon illustrating the carbon input and output fluxes (in g C km^{-1} yr^{-1}) at the Central America convergent margin. The inset shows the location of Mound 11 and Mound 12, ~30 km arcward from the Middle America trench. The total sedimentary carbon input to the margin is estimated at 1.6×10^9 g C km^{-1} yr^{-1} [*Li and Bebout*, 2005]. The carbon output through submarine fluid venting at the outer fore arc is 8.0×10^5 g C km^{-1} yr^{-1} (this study), and the volcanic front carbon flux derived from the subducted slab (i.e., marine carbonates and sedimentary organic carbon) is equal to ~1.9×10^8 g C km^{-1} yr^{-1} [*Hilton et al.*, 2002; *Shaw et al.*, 2003] (see section 5.3. for details). Subducted sediments do not represent a direct source of CO$_2$ to the back-arc region [*de Leeuw et al.*, 2007].

[2007] estimated the relative proportions of the three incoming sediment units required to satisfy the L/S ratio for the volcanic output in Costa Rica. They argued that the top 74 m section of the uppermost sediment unit (Unit U1) is not involved in supplying the output CO$_2$ flux to the volcanic front, and only the upper 19 m out of the total 290 m of the lowermost sediment unit (U3) are needed to maintain the required L/S ratio. Thus, most of Unit U3, together with the altered oceanic basement, is carried past the zone of arc magma generation. Consequently, the influence of subducting oceanic crust as a contributor to the volcanic carbon flux can be neglected. In contrast, a significant fraction of the uppermost unit (U1) of the downgoing sedimentary sequence is removed before reaching the zone of arc magma generation, consistent with the lack of a [10]Be signal in Costa Rica arc lavas [*Morris et al.*, 2002]. If this analysis is correct, then we suggest that the carbon content of the uppermost 74 m of Unit U1 alone, i.e., 6.9×10^7 g C km^{-1}yr^{-1} [*Li and Bebout*, 2005; *de Leeuw et al.*, 2007], represents the flux of carbon that is potentially available to supply the fore-arc region in Costa Rica.

[41] The total carbon emission from seep sites at the outer fore arc in Costa Rica can be estimated by combining the CO$_2$ flux observed in our study at

Mound 11a with estimates for the methane output from *Mau et al.* [2006]. As the entire margin offshore Nicaragua and Costa Rica has been extensively surveyed, and the distribution of seep sites well mapped [*Klaucke et al.*, 2008; *Ranero et al.*, 2008; *Sahling et al.*, 2008], we assume that our estimates encompass the major fraction of submarine carbon release. However, we caution that our CO$_2$ flux estimates are based on data from a single mound, and we exclude emissions from other seep structures (landslides, seamount subduction scars, and faults [*Sahling et al.*, 2008]). Furthermore, there is a significant temporal and spatial variability of measured carbon (CO$_2$ and methane) concentrations in seep fluids and in the water column at mud extrusions [*Mau et al.*, 2006, 2007]. Since fluid venting is highly variable both in space and in time, extrapolation of data from only one site may produce estimates with large uncertainties. In addition, CO$_2$- and methane-rich fluids might also be lost through channels in sediments and fractures in carbonates [*Mau et al.*, 2006] and/or via flow along the décollement zone toward the deformation front [*Kopf et al.*, 2000]; this fraction of the carbon output is not captured by our mass flux instruments on the seafloor. Also, methane may be stored in marine gas hydrates at continental margins [*Milkov et al.*, 2003], and a fraction of the (methane-derived) carbon likely

precipitates as authigenic carbonates at cold seep sites [*Han and Suess*, 1989; *Luff and Wallmann*, 2003] and/or is taken up by the seep biota [e.g., *Southward et al.*, 1981].

[42] In spite of these caveats, we can still derive first-order estimates of the methane-related carbon flux from the outer fore arc using the approach of *Mau et al.* [2006]. For the latest estimate of 77 mounds observed along a ~460 km long stretch of the continental slope at the Central America margin [*Klaucke et al.*, 2008; *Ranero et al.*, 2008; *Sahling et al.*, 2008], we calculate a total methane output of 3.1×10^7 mol/yr. This output estimate is based on average methane emissions (4×10^5 mol/yr [*Mau et al.*, 2006]) observed at four mounds (Mound 10, Mound 11, Mound 12, and Mound Culebra). This corresponds to a methane-related carbon flux equal to 8.0×10^5 g C $km^{-1}yr^{-1}$.

[43] For Mound 11, we calculate that the $\sum CO_2$ emission ranges from ~110 to 3100 mol/yr. This estimate is based on flow rates (2.7–25 cm/yr) and $\sum CO_2$ concentrations (0.15–0.34 cm^3 STP/g H_2O) observed during our 12 month deployment, combined with first-order estimates of the total area covered by bacterial mats (500–1700 m^2 [*Mau et al.*, 2006]) at the seep site. However, we note that for most of our record, flow rates are low (i.e., between 2 and 5 cm/yr), and the corresponding $\sum CO_2$ output then lies between ~110 and 800 mol/yr. Extrapolated over the 77 mound structures along the 460 km long section of the Central America margin, we estimate a maximum total CO_2 output of 2.4×10^5 mol/yr, corresponding to a carbon flux of 6.1×10^3 g C $km^{-1}yr^{-1}$. Notably, this value is two orders of magnitude less than the methane-related flux.

[44] Thus, the total carbon emission (CO_2 plus methane) from mounds at the Costa Rica margin is of the order of 8.0×10^5 g C $km^{-1}yr^{-1}$ (Figure 4). This flux represents ~1% only of the amount of carbon that is potentially available to the fore-arc region via the uppermost 74 m of sediment layer U1 (i.e., 6.9×10^7 g C $km^{-1}yr^{-1}$), assuming the analysis of *de Leeuw et al.* [2007]. Alternatively, compared to the total sedimentary carbon input to the subduction zone in Costa Rica (1.6×10^9 g C km^{-1} yr^{-1}; Figure 4 [*Li and Bebout*, 2005]), the carbon loss through fluid seepage at mound structures at the outer fore arc is virtually negligible. Consequently, we conclude that the submarine section of the Costa Rica fore arc does not represent a pathway for significant carbon loss from the subducting slab. Complementary studies are needed on the subaerial segment of the fore arc to assess the volatile release from the slab under more extreme P-T conditions.

6. Conclusions

[45] Our new He-CO_2 isotope and relative abundance results for submarine seep fluids allow us to assess the origin and fluxes of volatiles at the outer fore arc in Costa Rica. Elevated helium isotope ratios in fluids emanating at Mound 11, Mound 12 and Jaco Scar are consistent with a small but discernable component of mantle-derived helium. Mantle helium in this region may be derived from the lithospheric mantle segment of the subducting Cocos Plate or from oceanic igneous basement rocks related to the Galápagos hot spot or the CLIP. At the mounds, the carbon isotope composition of DIC shows that isotopically depleted methane and ^{13}C-enriched DIC produced by deep methanogenesis are carried from depth to the surface by upward flow of fluids derived from sediments of the subducting slab. Due to low fluid flow rates at Mound 12, most of the ascending dissolved methane is oxidized, resulting in extremely low $\delta^{13}C_{\sum CO2}$ values. In contrast, at the more active Mound 11, the ascending DIC is only slightly affected by biogeochemical processes in near-surface sediments.

[46] Through use of an innovative sampling approach coupling copper sampling coils to submarine flux meters, we are able to produce a quasi-continuous temporal record of the volatile chemistry of seep fluids emanating at Mound 11 and Mound 12. The remarkable temporal variability of the carbon and fluid emissions from the studied mounds demonstrates the necessity for long-term, continuous sampling in order to understand and quantify fluid and volatile emissions at submarine seep sites.

[47] We estimate that the carbon loss (CO_2 plus methane) through submarine fluid venting at mound structures at the Costa Rica fore arc is significantly less than the amount of carbon that is potentially available by subducted sedimentary input via the trench. Taken together, estimates of the carbon flux at the outer fore arc (this study), the volcanic front [*Hilton et al.*, 2002; *Shaw et al.*, 2003], and the back arc [*de Leeuw et al.*, 2007] at the Central America convergent margin represent ≤ ~12% of the total sedimentary carbon input into the subduction zone. Unless there is a significant but hitherto unidentified carbon flux at the inner fore arc, i.e., between the submarine fore arc and the volcanic front, our observations suggest that most of the carbon

entering the Costa Rica subduction zone must be recycled to the (deeper) mantle.

Acknowledgments

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