



## Nitrogen systematics and gas fluxes of subduction zones: Insights from Costa Rica arc volatiles

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[1] Volcanic gases are a powerful tool for assessing magmatic processes in subduction zones. We report gas chemistry and nitrogen isotope compositions of fumaroles, bubbling springs, and geothermal wells from the Costa Rican segment of the Central American volcanic segment (CAVS), and new correlation spectroscopy (COSPEC) SO<sub>2</sub> flux measurements of Poás and Arenal volcanoes. N<sub>2</sub>/He ratios (100–8,250) and nitrogen isotope compositions ( $\delta^{15}\text{N} = -3.02$  to  $+1.69\%$ ) of Costa Rica volatiles are consistent with sources ranging from typical arc-type end-members, with nitrogen addition from the subducting slab, to MORB end-member, having experienced no slab modification. Overall, nitrogen-helium chemistry of Costa Rican material indicates a diminished slab contribution versus other locations along the arc (e.g., Nicaragua and Guatemala). We use SO<sub>2</sub> flux measurements of Poás and Arenal ( $1.80 \cdot 10^5 \pm 4.00 \cdot 10^4$  and  $8.30 \cdot 10^3 \pm 4.00 \cdot 10^3$  kg/day, respectively, or  $1.30 \cdot 10^5 \pm 6.25 \cdot 10^4$  and  $2.81 \cdot 10^6 \pm 6.25 \cdot 10^5$  mol/day, respectively) to extrapolate a SO<sub>2</sub> flux for the Costa Rica segment of  $1.09 \cdot 10^9$  mol/day. Using CO<sub>2</sub>/S<sub>t</sub> (S<sub>t</sub> = total sulfur) of 2.7 and 5.9, we calculate CO<sub>2</sub> fluxes of  $1.88 \cdot 10^8$  and  $4.11 \cdot 10^8$  kg/yr, respectively ( $2.94 \cdot 10^9$  and  $6.42 \cdot 10^9$  mol/yr, respectively). Other volatile fluxes (N<sub>2</sub>, He, H<sub>2</sub>, Ar, HCl, and H<sub>2</sub>O) are calculated using CO<sub>2</sub>/S<sub>t</sub> and regional gas chemistry. For Costa Rica, the output/input ratios of nitrogen are less than unity (0.03 to 0.06 for CO<sub>2</sub>/S<sub>t</sub> of 2.7 and 5.9, respectively), suggesting more N is subducted than released in the subarc, possibly resulting from sediment offscraping, forearc devolatilization, limited fluid availability in the subarc, or subduction past the subarc.

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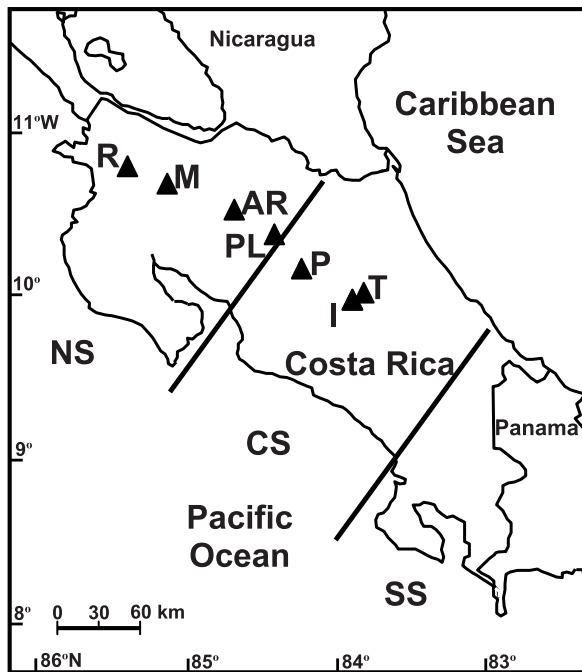
## 1. Introduction

[2] Fluids and volatiles released from the subducting slab are directly involved in fluxing the overlying mantle wedge and hence in the production of primary magmas [Tatsumi *et al.*, 1983; Arculus, 1994]. Defining their role in subduction zones is therefore a fundamental prerequisite in understanding processes of arc magma genesis and the growth of continental crust [e.g., Taylor and McLennan, 1985; Ellam and Hawkesworth, 1988]. In addition, subduction-related fluids and volatiles impart diagnostic geochemical signatures on arc volcanics so that subarc processes can be identified [e.g., Sano and Marty, 1995; Sano and Williams, 1996; Sano *et al.*, 2001; Hilton *et al.*, 2002]. Thus certain species can potentially be used as tracers for the presence of subducted components in the mantle source of arc volcanics.

[3] Recently, considerable emphasis has been placed on studying arcs from a mass balance perspective [Sano and Williams, 1996; Bebout, 1996; Plank and Langmuir, 1998; Sano *et al.*, 2001; Fischer *et al.*, 2002; Hilton *et al.*, 2002]. Mass balance models are not only critical to understanding subduction zone processes, but are also integral for understanding the chemical composition of the exosphere (crust, hydrosphere, and atmosphere) and the evolution of various mantle reservoirs, as well as determining the role

of volcanism in climate modeling. Successful application of the mass balance approach to subduction zones is contingent upon resolving the provenance of a particular element under scrutiny. By focusing on the isotopic composition of certain elements, problems associated with element provenance can usually be resolved [Varekamp *et al.*, 1992; Zhang and Zindler, 1993; Bebout, 1996; Sano and Williams, 1996; Plank and Langmuir, 1998; Patino *et al.*, 2000; Sano *et al.*, 2001; Fischer *et al.*, 2002; Hilton *et al.*, 2002; Snyder *et al.*, 2003].

[4] The Central American volcanic segment (CAVS) is an ideal location to assess mass balance because the arc has been extensively studied both from a geochemical and geophysical perspective [e.g., Carr *et al.*, 1990; Leeman *et al.*, 1994; Protti *et al.*, 1995; Patino *et al.*, 2000; von Huene *et al.*, 2000; Barckhausen *et al.*, 2001]. We present a detailed, systematic study of arc volatile characteristics in the Costa Rican segment of CAVS and use isotopic constraints to resolve N provenance into mantle, subducted sediment, and atmospheric components [Sano *et al.*, 1998, 2001; Fischer *et al.*, 2002; Hilton *et al.*, 2002]. In addition, we report new SO<sub>2</sub> flux measurements for Poás and Arenal volcanoes. Our estimated volatile flux of Costa Rica is compared to that of CAVS to examine Costa Rica's relative volatile contribution. In this way, the balance of volatile inputs from the subducting slab and volatile outputs via volcanic



**Figure 1.** Costa Rican segment of the Central American volcanic arc. Triangles indicate locations of active Costa Rican volcanoes; thick solid lines indicate geophysical segmentations of *Protti et al.* [1995]: NS (northern segment), CS (central segment), and SS (southern segment). R, Rincón de la Vieja; M, Miravalles; AR, Arenal; PL, Platanar; P, Poás; I, Irazú; T, Turrialba. Samples B, PS, and LM collected near Platanar; sample QN collected near Arenal (see Table 1).

degassing can be evaluated for this section of the arc.

## 2. Geological Background

[5] The Central American volcanic segment is the result of subduction of the Cocos Plate beneath the Caribbean Plate, with Costa Rica representing the southernmost occurrence of active volcanism in the arc (Figure 1). Convergence is nearly orthogonal at  $\sim 90$  mm/yr [*Protti et al.*, 1995]. Subduction zone geometry in Costa Rica is complex and can be divided into northern, central, and southern segments (Figure 1) [*Protti et al.*, 1995].

[6] The northern segment is characterized by a steep slab dip ( $80^\circ$  at depths  $>100$  km) and subduction of 25–30 Ma old oceanic crust that was generated at the East Pacific Rise (EPR) [*Protti et al.*, 1995]. The central segment has a shallower slab

dip ( $60^\circ$  at depths  $>100$  km), subducting younger crust (20–22 Ma) generated at the Cocos-Nazca spreading center [*Protti et al.*, 1995]. The boundary between the northern and central segments has been termed the “rough-smooth boundary” [*Hey*, 1977] to reflect the smooth nature of EPR crust, and the rough texture of crust from the Cocos-Nazca spreading center (due to isolated seamounts generated at the Galapagos hot spot). *Protti et al.* [1995] suggested there is a tear in the subducting Cocos Plate at the division between the northern and central segments, likely a relic fracture along which the Farallon plate broke into the Cocos and Nazca plates. The thickness of the overlying Caribbean crust varies between the northern (36–38 km) and central (41–45 km) segments [*Carr and Stoiber*, 1990]. Arc volcanism ceases near the center of the central segment ( $N83^\circ W55^\circ$ ).

[7] Systematic geochemical variations have been recognized along the strike of CAVS [e.g., *Carr et al.*, 1990; *Morris et al.*, 1990; *Leeman et al.*, 1994; *Patino et al.*, 2000]. Trace element and cosmogenic isotope ratios (e.g., Ba/La, B/La, and  $^{10}\text{Be}/^9\text{Be}$ ) vary considerably along CAVS, with Nicaragua displaying the highest ratios (corresponding to greater slab and/or sediment contributions), Costa Rica the lowest, and Guatemala and El Salvador being intermediate. *Leeman et al.* [1994] suggested low B/La in central Costa Rica is the result of shallow release of fluid-mobile elements due to warmer, shallower subduction of the Cocos Plate. Steeper subduction and cooler thermal regimes further northwest along the arc result in B retention until the subarc. *Leeman et al.* [1994] also attribute low  $^{10}\text{Be}/^9\text{Be}$  in Costa Rica to regional underplating of the uppermost meters of the subducting sediment column [*Shiple et al.*, 1990]. Alternatively, *Morris et al.* [2002] note that sediment erosion of the overlying crust [*Shiple and Moore*, 1986] could dilute the  $^{10}\text{Be}/^9\text{Be}$  signal in the sediment profile, also resulting in low  $^{10}\text{Be}/^9\text{Be}$  in erupted magmas.

[8] Along-arc geochemical variations have also been observed in volatile compositions. *Fischer et al.* [2002] showed that N isotopes and  $\text{N}_2/\text{He}$  ratios in geothermal fluids vary between Guatemala and Costa Rica. Nitrogen isotope compositions of Guatemala indicate a dominantly subducted sedi-

mentary N source, while those for Costa Rica indicate a dominantly mantle wedge source. *Snyder et al.* [2001] report  $\text{CO}_2/{}^3\text{He}$  variations along the arc, with highest ratios displayed in Costa Rica and lowest ratios in Guatemala. They attributed the difference to variations in subduction parameters; for example, the subducting plate beneath Costa Rica is younger (and therefore warmer) and subducting at a shallower angle than the plate subducting further north along the arc. The warmer thermal regime of Costa Rica may enhance decarbonation and lead to elevated  $\text{CO}_2/{}^3\text{He}$ . *Shaw et al.* [2003] examined carbon and helium systematics in Costa Rica and Nicaragua and observed similar  $\text{CO}_2/{}^3\text{He}$  values for these two segments of the arc. The proportion of C derived from limestone and marine carbonate relative to the proportion derived from organic sediment is also similar in both segments ( $\sim 10:1$ ). However, the ratio of slab-derived carbon (limestone, marine carbonate, and organic sediments) to mantle carbon was substantially greater in Nicaragua, consistent with a higher sedimentary flux to arc volcanics in this region.

### 3. Sampling and Analytical Procedures

[9] Fumarole, bubbling spring, and geothermal well samples were collected in evacuated 200 ml Pyrex flasks, filled with 60–80 ml 5N NaOH (samples collected by TPF, MMZ, and DRH). Samples from geothermal wells were collected using a steam separator. *Giggenbach and Goguel* [1989] and *Hilton et al.* [2002] provide a detailed description of collection procedures.

[10] The composition of the headspace gases (He,  $\text{H}_2$ , Ar,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ , CO) was determined using gas chromatography after *Giggenbach and Goguel* [1989] and *Zimmer* [2002] in the University of New Mexico Volcanic and Geothermal Fluid Analysis Laboratory. Argon and oxygen are not separated by the 5Å molecular sieve column, so an oxygen trap was used to remove  $\text{O}_2$  in order to detect Ar abundance. For samples that contained  $>0.16$  mmol  $\text{O}_2/\text{mol}$  total gas (7 out of 27 samples), the trap became saturated and a quantity of  $\text{O}_2$  was detected along with Ar. Analyses of air at various pressures show that the proportion of oxygen

removed was constant. Thus the Ar value of the air can be calculated using the following equation:

$$\text{Ar}_c = \left( \frac{N_2}{\text{Ar}} * \frac{1}{N_{2,m}} \right)^{-1} \quad (1)$$

where  $\text{N}_2/\text{Ar}$  is 83.6 (the volume ratio of  $\text{N}_2/\text{Ar}$  in dry air),  $N_{2,m}$  is  $\text{N}_2$  measured during the analysis of air, and  $\text{Ar}_c$  is the corrected Ar value. The corrected Ar value was plotted against the measured Ar value, resulting in a linear correlation. The equation governing the correlation was then used to correct Ar values of samples with  $\text{O}_2 > 0.16$  mmol/mol. Samples that have been corrected are denoted by a “+” following the Ar number (Table 1). Oxygen was analyzed separately using Ar carrier gas, so separation of the species is unnecessary.

[11] Gases present in the caustic solution were analyzed using wet chemistry and precipitation techniques after *Giggenbach and Goguel* [1989]. Variations in chemistry due to sampling and analytical procedures are discussed in *Giggenbach and Matsuo* [1991] and *Giggenbach et al.* [2001].

[12] Nitrogen isotope analyses were performed at the University of New Mexico Stable Isotope Laboratory using a Finnigan Delta Plus XL stable isotope mass spectrometer with a Finnigan Mat Gas Bench interface. Aliquots of headspace gas were collected in soda glass breakseals. For analysis, a rubber septum was placed on the end of a breakseal, and the headspace was evacuated. The septum was then pierced with a two-hole needle. Helium carrier gas entered the headspace via the needle at a flow rate of 0.5 ml/min. Remaining headspace gas (air) was sampled by the mass spectrometer until no nitrogen peak was detected, assuring that the headspace was purged. Once the headspace was purged, the breakseal was broken. Sample gas was carried through a NAFION™ tube for water removal by He carrier gas at a flow rate of 0.5 ml/min. Sample gas was loaded into a 50  $\mu\text{l}$  sample loop on a six-port valve, then injected at a flow rate of 2 ml/min. To prevent backflow of air through the vent, a large volume was placed on the vent-side of the valve and allowed to fill with He carrier gas. The sample was run after pressure inside the breakseal exceeded atmospheric. After injection, sample gas entered a Hayes Sep D 2m 5Å molecular sieve gas chromatography



**Table 1.** Gas Compositions of Costa Rica Geothermal Systems<sup>a</sup>

Location	Sample ID	Alternate Sample ID	Date (mm-dd-yy)	Type	Latitude	Longitude	Temp, °C	CO <sub>2</sub>	S <sub>t</sub>	SO <sub>2</sub>	H <sub>2</sub> S	
Turrialba Volcano	T1	CR-2	01-04-01	FC	N 10°01.156'	W 083°45.937'	89.6	13.6	0.09	0.09	n.d.	
	T2	CR-3	01-04-01	FC	N 10°01.156'	W 083°45.937'	89.6	10.7	0.19	0.19	n.d.	
	T3	CR2-1	03-10-01	FC	N 10°01.156'	W 083°45.937'	89.7	15.2	0.04	n.d.	0.04	
	T4		03-10-01	FC	N 10°01.156'	W 083°45.937'	89.7	13.7	0.07	0.05	0.02	
	T5	CR3-2	07-07-01	FC	N 10°01.156'	W 083°45.937'	84.2	41.9	26.5	25.7	0.83	
Irazú Volcano (duplicate)	I1	CR-4	01-05-01	FF	N 09°59.723'	W 83°47.308'	88.5	43.6	2.51	0.00	2.51	
	I2	CR-5	01-05-01	FF	N 09°59.723'	W 83°47.308'	88.5	41.3	2.51	0.05	2.46	
Poás Volcano	P1	CR-6	01-06-01	FC	N 10°11.883'	W 84°13.719'	76.0	8.00	1.08	n.d.	1.08	
	P2	CR-8	01-06-01	FC	N 10°11.883'	W 84°13.719'	76.0	8.25	1.09	0.92	0.17	
	P3	CR-9	01-06-01	FC	N 10°11.883'	W 84°13.719'	76.0	12.0	1.03	0.82	0.21	
	P4	CR2-6	03-12-01	FC	N 10°11.883'	W 84°13.719'	n.m.	42.0	4.95	3.00	1.95	
	P5		03-12-01	FC	N 10°11.883'	W 84°13.719'	92.2	9.44	1.60	1.47	0.13	
	P6	CR3-17	03-12-01	FC	N 10°11.883'	W 84°13.719'	n.m.	3.30	0.71	0.46	0.25	
	P7		07-08-01	FC	N 10°11.883'	W 84°13.719'	92.8	13.5	6.79	6.59	0.20	
	P8	07-14-01	FC	N 10°11.883'	W 84°13.719'	108	3.37	7.89	5.72	2.17		
Chacocuella-Platanar volcanic system	B1	CR-11	01-08-01	SF	N 10°21.072'	W 84°13.279'	n.m.	443	0.68	0.68	n.d.	
Bajos del Toro	B2	CR-13	01-08-01	SF	N 10°21.072'	W 84°13.279'	n.m.	228	0.40	0.40	n.d.	
Bajos del Toro (duplicate)	LM	CR-14	01-08-01	SF	N 10°21.072'	W 84°13.279'	46.0	95.8	0.30	0.14	0.16	
La Marina	PS	CR-15	01-09-01	SF	N 10°21.087'	W 84°40.534'	59.5	486	0.41	0.09	0.32	
Arenal volcanic system	QN	CR-16	01-10-01	SF	N 10°29.720'	W 84°21.804'	n.m.	354	3.56	2.95	0.61	
Quebrada Naranja	MH	CRT-9	01-11-01	MF	N 10°42.777'	W 85°10.638'	88.6	101	0.57	0.05	0.52	
Miravalles volcanic system			M1	01-12-01	WF	N 10°41.907'	W 85°11.799'	238 <sup>b</sup>	2.03	0.04	n.d.	0.04
Miravalles power plant			M2	01-12-01	WF	N 10°42.309'	W 85°11.630'	233 <sup>b</sup>	0.25	0.01	n.d.	0.01
Miravalles power plant	Rincón de la Vieja volcanic system	CR-21	01-12-01	MF	N 10°46.372'	W 85°20.652'	83.3	286	2.77	0.80	1.97	
Las Pailas		R1	01-12-01	SF	N 10°46.372'	W 85°20.652'	65.3	34.9	5.64	5.64	n.d.	
Las Pailas		R2	01-12-01	MF	N 10°46.372'	W 85°20.652'	n.m.	425	3.66	2.61	1.05	
Las Pailas		R3	03-18-01	MF	N 10°46.372'	W 85°20.652'	81.3	2.03	0.08	0.04	0.04	
Borinquen	RB	CR-24	01-13-01	MF	N 10°48.588'	W 85°24.782'						





**Table 1.** (continued)

Location	Sample ID	HCl	HF	He	H <sub>2</sub>	Ar	N <sub>2</sub>	N <sub>2,exc</sub>	NH <sub>3</sub> (*10 <sup>-4</sup> )	O <sub>2</sub>	CH <sub>4</sub>	CO (*10 <sup>-4</sup> )	H <sub>2</sub> O
<i>Turrialba Volcano</i>	T1	0.25	0.01	0.00016	0.0196	0.0007	0.102	0.08	0.02	<0.0001	0.00001	0.09	986
	T2	0.29	0.01	0.00017	0.0221	0.0008	0.113	0.08	0.01	<0.0001	0.00001	0.03	989
	T3	0.33	0.01	0.00008	0.0104	0.0009	0.068	0.03	0.01	0.0024	0.00001	0.06	984
	T4	0.18	0.01	0.00012	0.0155	0.0015	0.111	0.05	0.01	0.0007	0.00001	0.08	986
	T5	1.60	0.37	0.00088	0.0028	0.0109	1.152	0.72	0.40	0.9010	0.00005	0.57	551
<i>Irazú Volcano</i>	I1	0.15	0.04	0.00051	0.0038	0.0020	0.673	0.59	0.01	<0.0001	0.00001	0.07	953
	I2	0.10	0.04	0.00036	0.0003	0.0017	0.538	0.47	n.d.	0.0150	0.00007	0.04	956
<i>Poás Volcano</i>	P1	0.18	0.01	0.00020	0.0476	0.0003	0.021	0.01	0.01	<0.0001	<0.00001	0.43	991
	P2	0.56	0.01	0.00021	0.0572	0.0003	0.031	0.02	0.01	<0.0001	<0.00001	0.56	990
	P3	0.32	0.01	0.00024	0.0100	0.0003	0.026	0.01	0.01	0.0001	<0.00001	0.35	987
	P4	19.5	1.12	0.00127	0.1069	0.4049 <sup>c</sup>	23.02	6.82	0.88	4.9666	<0.00030	<2.90	904
	P5	0.20	0.01	0.00009	0.0026	0.0003	0.023	0.01	n.d.	0.0017	<0.00001	0.14	989
	P6	2.40	0.01	0.00007	0.0494	0.0623 <sup>c</sup>	3.456	0.96	0.03	0.5336	<0.00001	0.97	989
	P7	0.33	0.02	0.00010	0.0055	0.0007	0.038	0.01	0.01	0.0063	<0.00001	1.16	979
	P8	0.99	0.01	0.00014	0.0045	0.0004	0.021	0.01	n.d.	0.0026	<0.00001	0.41	988
<i>Chacosuela-Platanar volcanic system</i>													
Bajos del Toro	B1	2.51	0.44	0.00069	0.0020	0.1462 <sup>c</sup>	3.836	0.00	0.12	<0.0007	0.00049	<0.21	914
	B2	1.65	0.22	<0.00001	0.0002	0.0876 <sup>c</sup>	2.505	0.00	0.07	1.3905	0.00052	<0.19	923
	LM	2.55	0.36	0.00317	0.0003	0.0700	15.743	12.9	0.07	0.2612	0.22726	<0.22	914
Poco Sol. Phys.,	PS	4.79	0.28	0.00584	0.2906	0.1211	12.686	7.84	0.11	0.1499	9.42214	<0.45	486
<i>Arenal volcanic system</i>													
Quebrada Naranja	QN	7.21	0.57	0.00457	0.0041	0.0851 <sup>c</sup>	8.321	4.92	0.20	1.3269	40.5026	<1.17	708
<i>Miravalles volcanic system</i>													
Homillas	MH	0.40	0.04	0.00025	0.1394	0.0039	0.392	0.23	n.d.	<0.0001	0.20290	0.34	897
Miravalles power plant	M1	0.11	0.01	0.00003	0.0025	0.0042 <sup>c</sup>	0.754	0.58	0.02	0.1599	0.00065	<0.01	997
Miravalles power plant	M2	0.13	0.01	<0.00001	0.0002	0.0013	0.078	0.03	n.d.	<0.0001	0.00016	<0.01	999
<i>Rincón de la Vieja volcanic system</i>													
Las Pailas	R1	10.5	0.59	0.00256	1.6782	0.6779 <sup>c</sup>	63.44	36.3	0.88	9.2676	0.20203	<1.60	984
Las Pailas	R2	3.38	0.41	0.00081	2.2177	0.2158	10.24	1.60	0.08	0.0234	0.35691	12.7	920
Las Pailas	R3	3.73	0.44	0.00081	0.9698	0.1089	6.683	2.32	0.15	0.0134	0.13092	7.93	558
Borinquen	RB	0.14	0.01	0.00002	0.0378	0.0043	0.390	0.22	0.01	0.0054	0.00259	<0.01	813

<sup>a</sup> Costa Rica gas compositions (mmol/mol). Alternate Sample ID is sample ID used by *Shaw et al.* [2003]. For first letter of sample type: F, fumarole; S, bubbling spring; M, bubbling mudpot; W, geothermal well. Second letter: C, summit crater; F, flank; n.m., not measured; n.d., not detected.

<sup>b</sup> Temperature at depth.

<sup>c</sup> Corrected for Ar (see text); N<sub>2,exc</sub> = N<sub>2</sub> - 40\*Ar.

**Table 2.** N<sub>2</sub>/He ratios, Nitrogen Isotope Compositions, and M-S-A Calculations for Costa Rica Geothermal Fluids<sup>a</sup>

Volcano	Sample	N <sub>2</sub> /He	δ <sup>15</sup> N, ‰	M	S	A	%S <sup>b</sup>
Turrialba	T1	643	0.4 ± 0.3 <sup>d</sup>	0.23	0.27	0.50	54
Turrialba	T3 <sup>c</sup>	866	-1.0 ± 0.3 <sup>c</sup>	0.17	0.00	0.83	0
Irazú	I2	1483	1.7 ± 0.4 <sup>d</sup>	0.09	0.39	0.51	81
Poás	P1	101	-1.9 ± 0.3 <sup>d</sup>	–	–	–	–
Poás	P5	268	-2.7 ± 0.4 <sup>d</sup>	0.56	0.01	0.43	2
Poás	P7 <sup>c</sup>	373	-2.4 ± 0.5 <sup>d</sup>	0.40	0.00	0.60	0
Poás	P8 <sup>c</sup>	156	-3.0 ± 0.6 <sup>d</sup>	0.83	0.17	0.00	17
Bajos del Toro	B1	5587	0.7 ± 0.3	0.02	0.15	0.83	86
Miravalles	MH	1547	-0.1 ± 0.4	0.10	0.07	0.83	33
Miravalles	M1 <sup>c</sup>	25,419	-0.1 ± 0.4	0.01	0.00	0.99	0
Rincón de la Vieja	R1	25,787	-0.7 ± 0.6	–	–	–	–
Rincón de la Vieja	R3	8248	-2.1 ± 0.4	–	–	–	–
Endmember compositions							
Mantle		150 <sup>e</sup>	-5 <sup>g</sup>				
Sediment		10,500 <sup>d</sup>	5.5 <sup>h</sup>				
Air		148,900 <sup>f</sup>	0 <sup>i</sup>				

<sup>a</sup> Nitrogen isotope values and M-S-A calculations for Costa Rica gases, after *Sano et al.* [2001]. M, mantle; S, sediment; A, air.

<sup>b</sup> %S = 100\*S/(M + S).

<sup>c</sup> Samples that fall slightly outside of mixing lines were moved to intersect mixing lines by increasing N<sub>2</sub>/He or δ<sup>15</sup>N; alternate values used in mixing equations are listed in (N<sub>2</sub>/He, δ<sup>15</sup>N) format with the altered number in bold: T3 (866, **-0.9‰**); P7 (373, **-2.0‰**); P8 (**181**, **-3.0‰**); M1 (25,420, **0.0‰**). Samples P1, R1, and R3 fall outside the mixing lines of M-S-A in Figure 5 and cannot be resolved into the 3-component mixing system.

<sup>d</sup> From *Fischer et al.* [2002].

<sup>e</sup> *Marty and Zimmerman* [1999].

<sup>f</sup> *Ozima and Podosek* [2002].

<sup>g</sup> *Marty* [1995].

<sup>h</sup> *Li et al.* [2003].

<sup>i</sup> Air is referenced at 0‰.

graphic column, followed by a second NAFION™ water trap, then to the mass spectrometer. Reported N isotope values are the average of 4–17 analyses of the same gas aliquot. Errors are calculated by error propagation of 1σ standard deviations of the sample and the reference (air); errors range from 0.3 to 0.6‰ (Table 2). For air analyses, air was collected from various locations indoors and outdoors in a glass tube, sealed with a rubber septum, and analyzed immediately.

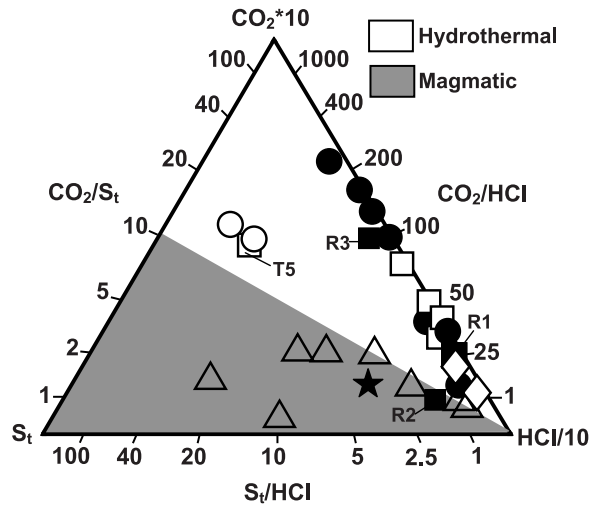
## 4. Results

[13] We report volatile chemistry associated with geothermal activity at the following volcanic systems in Costa Rica: Irazú, Turrialba, Poás, Chacocuella-Platanar, Arenal, Miravalles, and Rincón de la Vieja (Table 1). Gaseous plumes were visible at Poás and Arenal volcanoes.

### 4.1. Acid Gases

[14] Aside from water, the three major components of volcanic gases are CO<sub>2</sub>, S<sub>t</sub> (total sulfur), and HCl

(Table 1, Figure 2). Gases associated with arc-related volcanic-magmatic origins tend to have relatively higher S<sub>t</sub> and HCl contents and generally CO<sub>2</sub>/S<sub>t</sub> < 10. Hydrothermal gases are characterized by CO<sub>2</sub>/S<sub>t</sub> > 10 [*Symonds et al.*, 1994; *Giggenbach*, 1996]. Higher ratios of hydrothermal gases are the result of S partitioning into the hydrothermal system as H<sub>2</sub>SO<sub>4</sub>, so samples with higher CO<sub>2</sub>/S<sub>t</sub> indicate secondary hydrothermal alteration of the magmatic S. Variation in the HCl content of low temperature gas emissions is also due to secondary processes, such as the absorption and release of chlorine from the hydrothermal system [*Giggenbach*, 1996]. Magma degassing may also affect S<sub>t</sub>/HCl. *Symonds et al.* [1996] showed that Cl/S of high temperature fumaroles (>650°C) at Showa-Shinzan dome increased by a factor of ~3 from the mid 1950's to the mid 1960's, and ascribed this observation to degassing of a batch of magma over time. However, effects of degassing are minor in comparison to effects of gas-hydrothermal interaction for our samples because (1) they were collected from low-temperature systems and (2) sampling



**Figure 2.** Triangular diagram illustrating relationships between  $\text{CO}_2$ - $\text{S}_t$ -HCl for Costa Rica fumaroles, bubbling springs, and geothermal well samples. Open squares are Turrialba; open circles are Irazú; open triangles are Poás; open diamonds are Miravalles geothermal wells; filled circles are bubbling springs; filled squares are Las Pailas, Rincón de la Vieja; filled star is average composition of Momotombo ( $T > 800^\circ\text{C}$ ), Nicaragua (Menyailov *et al.* [1986], shown for reference). Abbreviations as in Table 1. Costa Rica volatiles are predominantly hydrothermal, with the exception of samples from Poás and R3.

occurred over a short timescale (months), where seasonal variations are most significant.

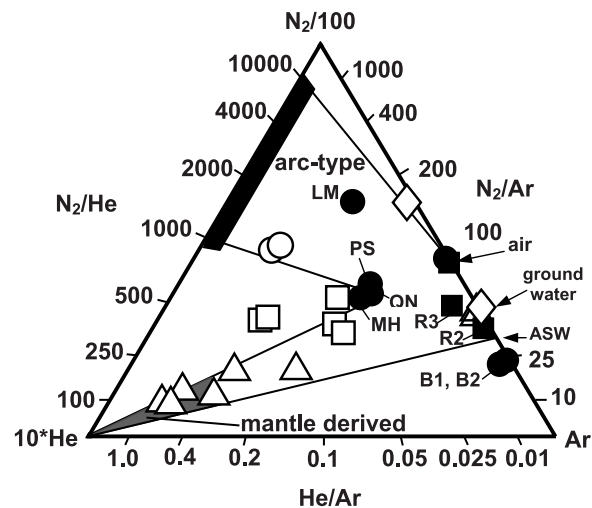
[15] From the present sample suite, only Poás plots in the field of magmatic gases. Large variations in  $\text{CO}_2/\text{S}_t$  and  $\text{S}_t/\text{HCl}$  at Poás over the seven-month sampling period are related to seasonal changes in the amount of surface water infiltrating the hydrothermal system as well as precipitation or remobilization of elemental sulfur [Zimmer *et al.*, 2002]. Irazú samples plot in the hydrothermal field, with  $\text{CO}_2/\text{S}_t$  of  $\sim 16$ . Turrialba samples show a range in  $\text{CO}_2/\text{HCl}$  during the seven-month sampling period with consistently low  $\text{S}_t/\text{HCl}$  ( $< 1$ ); the exception being sample T5 ( $\text{S}_t/\text{HCl}$  of  $\sim 40$ ) which was collected at a different location than samples from January and March, 2001. Fumaroles from the same volcano frequently exhibit variations from one locality to another [Giggenbach *et al.*, 1990; Fischer *et al.*, 1997].

[16] Gases from bubbling springs plot in the hydrothermal field of Figure 2. Sulfur is usually present

as  $\text{H}_2\text{S}$  in hydrothermal samples, but B1, B2 (Bajos del Toro) and R2 (Rincón de la Vieja), have sulfur entirely present as  $\text{SO}_2$ . Oxidation of sulfur may result from interaction with air-saturated groundwater near the surface, as these samples plot near the air-saturated water end-member in Figure 3 (see below). Rincón de la Vieja samples also display a range in  $\text{S}_t/\text{HCl}$  contents between locations, where R2, collected from a different site than R1 and R3, displays a higher  $\text{S}_t/\text{HCl}$ . R1 and R3, collected from the same location in January and March 2001, respectively, display an order of magnitude range in  $\text{CO}_2/\text{HCl}$ . The variability in  $\text{S}_t/\text{HCl}$  and  $\text{CO}_2/\text{HCl}$  may result from HCl partitioning into condensed steam in the sampling tube [Giggenbach and Matsuo, 1991]. In addition, it is possible that water from the bubbling pools at Las Pailas was entrained in the sample. Taran *et al.* [1998] attribute unusually high HCl contents of hydrothermal gases from El Chichon, Mexico, to droplets of saline water from the pool entering the sampling flask.

#### 4.2. Nonreactive Gases

[17] While plotting the relative proportions of  $\text{CO}_2$ ,  $\text{S}_t$ , and HCl provides a broad sample classification, the relative proportions of inert species  $\text{N}_2$ , He, and Ar characterize the provenance of these volatiles.



**Figure 3.** Triangular plot depicting relative abundances of inert gases  $\text{N}_2$ , He, and Ar. Also shown: air, groundwater (meteoric), air-saturated water (ASW). Abbreviations as in Table 1; symbols as in Figure 2. Samples from Poás and Turrialba have lower  $\text{N}_2/\text{He}$  than typical arc-related gases. After Giggenbach [1992].



The high proportion of N<sub>2</sub> and Ar in the atmosphere allows the distinction of air-contaminated samples, and N<sub>2</sub>/He ratios are useful in distinguishing mantle-derived versus arc-type samples. Gases dominated by a mantle-derived component (MORB or OIB) have low N<sub>2</sub>/He of 10–150 [Matsuo *et al.*, 1978; Giggenbach, 1992; Marty and Zimmerman, 1999; Fischer *et al.*, 2003], whereas gases from volcanic arcs are distinguished by higher N<sub>2</sub>/He (800–10,000 [Giggenbach, 1996; Fischer *et al.*, 1998; Sano *et al.*, 2001]).

[18] The only samples in Costa Rica with arc-type N<sub>2</sub>/He are from Irazú volcano. Most of the samples from Poás have low N<sub>2</sub>/He, consistent with mantle derivation; the exception being samples P4 and P6, which have been contaminated by air-saturated groundwater. Fumarolic gases from arc volcanoes seldom plot in the mantle-derived field, so the results from Poás are unusual (Figure 3). There are some observations of a shift in fumarolic N<sub>2</sub>/He from the arc-type to the mantle-derived field days to weeks before or after an eruption has been observed, possibly related to the injection of new, basaltic magma [Fischer *et al.*, 1997]. However, samples collected at Poás from January to July 2001 all plot in the mantle-derived field and have low N<sub>2</sub>/He (<300) similar to MORB- or OIB-derived volatiles [Matsuo *et al.*, 1978; Giggenbach, 1992; Fischer *et al.*, 2003]. Similar ratios were measured on samples collected in March 2003 (Fischer, unpublished results), without any eruptive behavior observed at the volcano.

[19] Turrialba samples have N<sub>2</sub>/He intermediate between those of Irazú and Poás. Samples that plot along the N<sub>2</sub>/Ar axis (R1, R2, RB; Rincón de la Vieja) have been overwhelmed by air or air-saturated water (ASW). Samples B1 (Bajos del Toro) and R3 (Rincón de la Vieja) plot near the N<sub>2</sub>/Ar axis but have N<sub>2</sub>/He of 5,600 and 8,250, respectively, thus they have (at least partly) retained a nonair signature. Other samples (LM, PS, QN, and MH) have N<sub>2</sub>/He of 1,000–2,000 and nonair He/Ar (>0.025). The N<sub>2</sub>/He and He/Ar values of these samples indicate either arc- or mantle-derived gases that have shifted toward ASW or air.

[20] We use N<sub>2</sub>/Ar to monitor air contamination. Both gases are present in minor amounts in the

mantle, but are significant components of air [Matsuo *et al.*, 1978]. Nitrogen present in excess of air (N<sub>2-exc</sub>; Table 1) is calculated using the following equation [Giggenbach, 1995; Fischer *et al.*, 1998]:

$$X_{N_2-exc} = X_{N_2,m} - 40 * X_{Ar,m} \quad (2)$$

where  $X_{N_2,m}$  and  $X_{Ar,m}$  are the measured concentrations of N<sub>2</sub> and Ar in a sample, respectively, and 40 is the N<sub>2</sub>/Ar of air saturated water [Heaton and Vogel, 1981]. Nitrogen/Ar of air saturated water, rather than air, is used to calculate N<sub>2-exc</sub> because it is the most likely form of contamination. Air does not enter the flask during sampling; otherwise, the flask would quickly fill, but this was not the case for the samples we collected. High <sup>4</sup>He/<sup>20</sup>Ne of samples collected at the same time, using the same sampling tubes, also indicate very little air contamination [Shaw *et al.*, 2003]. Although it cannot be ruled out that some Ar comes from air directly, air saturated water is a much more likely candidate.

[21] Samples with high O<sub>2</sub> that were corrected for Ar yield high N<sub>2-exc</sub> values, yet the presence of O<sub>2</sub> in the samples indicates that they are air contaminated and should contain little or no N<sub>2-exc</sub>. This discrepancy suggests the calculated N<sub>2-exc</sub> values of samples that have been corrected for Ar are too high because the correction based on the measured Ar is too large.

### 4.3. Nitrogen Isotopes

[22] Nitrogen isotope ratios for 12 samples are reported in Table 2. In addition to 7 previously reported results [Fischer *et al.*, 2002], we present new  $\delta^{15}N$  values from the northern and central segments, including Bajos del Toro, Miravalles, and Rincón de la Vieja. Samples from the central segment span the entire range of N isotope values observed in Costa Rica (−3.0 to +1.7‰, from Poás and Irazú, respectively). Nitrogen isotope compositions of nonair contaminated samples (N<sub>2-exc</sub> > 0) from the northern segment cluster around 0.0‰ or are negative. The geothermal well sample from Miravalles (M1; PGM 45) shows evidence of extreme air contamination

( $N_2/He > 25,000$ ,  $He/Ar < 0.1$ , no  $N_{2-exc}$ , and  $\delta^{15}N = 0\%$ ). Sample R3 has a negative isotopic value ( $-2.1\%$ ), similar to what is observed at Poás volcano.

#### 4.4. SO<sub>2</sub> Flux

[23] Sulfur dioxide flux was measured at Poás and Arenal volcanoes in March 2001, using the ground-based stationary COSPEC technique [Stoiber *et al.*, 1983]. Repeated scans were made at both locations to account for variations in flux. Twenty-eight scans were made at Poás, and twelve at Arenal. Plume speed was determined by tracking a horizontally moving parcel of the plume and timing the movement (average velocity = 1.2 m/s for both locations). The largest error of the calculation is plume speed determination; a detailed discussion of errors is given by Stoiber *et al.* [1983]. The measured fluxes are  $8.30 \cdot 10^3 \pm 4.00 \cdot 10^3$  and  $1.80 \cdot 10^5 \pm 4.00 \cdot 10^4$  kg/day ( $1.30 \cdot 10^5 \pm 6.25 \cdot 10^4$  and  $2.81 \cdot 10^6 \pm 6.25 \cdot 10^5$  mol/day) for Poás and Arenal, respectively.

### 5. Discussion

[24] Quantifying the amount of gaseous species emitted from subduction zone volcanoes, and resolving the total flux into juvenile and recycled components, is vital to understanding the geochemical mass balance of the crust and mantle [Sano and Williams, 1996; Sano *et al.*, 2001; Hilton *et al.*, 2002]. In this section, we focus on resolving N provenance, quantifying volatile fluxes, and assessing N mass balance for the Costa Rican segment of CAVS.

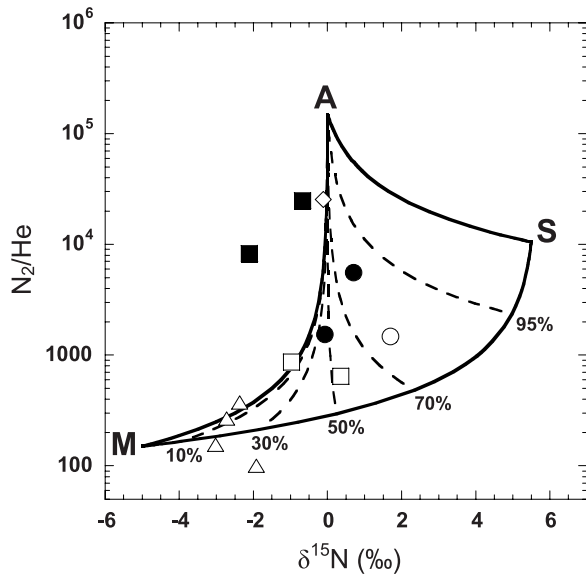
#### 5.1. Nitrogen Sources

[25] Before examining N systematics in detail, the data must be scrutinized to eliminate samples contaminated by air and crustal volatiles. Owing to the high atmospheric abundance of nitrogen and argon,  $N_2/He$ ,  $N_2/Ar$  and  $He/Ar$  are particularly sensitive to atmospheric contamination. Figure 3 and Table 2 show that samples with  $N_2/Ar$  close to air (83) or ASW (40), and  $He/Ar < 0.01$ , also have high  $N_2/He (>25,000)$ . These

criteria eliminate M1, (Miravalles) and R1 (Rincón de la Vieja) as air-contaminated. Crustal contamination can be evaluated using  $^3He/^4He$ , given the large difference between radiogenic (crustal) values ( $^3He/^4He \sim 0.05R_A$ , where  $R_A$  is the  $^3He/^4He$  of air,  $1.4 \cdot 10^{-6}$ ), compared to the mantle (as sampled by MORB;  $8.0R_A \pm 1.0R_A$ ). The worldwide average of arc  $^3He/^4He$  is  $5.4R_A$  [Hilton *et al.*, 2002]. However, this average includes some samples with low (crustally contaminated)  $^3He/^4He$  values. Eliminating samples with  $^3He/^4He$  significantly less than  $5.4R_A$  should remove suspect samples. Samples from Bajos del Toro ( $^3He/^4He [R_C/R_A] = 1.04$ ), La Marina ( $^3He/^4He [R_C/R_A] = 2.53$ ) and to a lesser extent the Miravalles geothermal well ( $^3He/^4He [R_C/R_A] = 5.20$  [Shaw *et al.*, 2003]) show evidence of crustal addition, thus they are not considered to represent the underlying magmatic source of volatiles. Air and crustally contaminated samples identified here are not incorporated in the following calculations and discussion.

[26] In subduction zones, potential N sources include the mantle wedge, subducting crust and sediments, and air [Sano *et al.*, 2001]. High  $N_2/He$  (800–8,000 in arcs vs. 10–150 in MORB [Marty, 1995; Giggenbach, 1992; Marty and Zimmerman, 1999; Sano *et al.*, 2001]) have been ascribed to the addition of N from subducted marine sediments [Giggenbach, 1992; Kita *et al.*, 1993; Fischer *et al.*, 1998; Sano *et al.*, 2001; Fischer *et al.*, 2002]. The addition of sedimentary N is further supported by isotopic analyses revealing that nitrogen emitted from arcs has higher  $^{15}N/^{14}N$  than MORB [Sano *et al.*, 2001; Fischer *et al.*, 2002]. With reference to air ( $\delta^{15}N = 0.0\%$ ), mantle nitrogen, as measured in fresh MORB glass samples, has an isotopic composition of  $-5\%$  ( $^{15}N/^{14}N$  in per mil notation [Marty, 1995]). Marine sediments have a nitrogen isotope composition of  $+7 \pm 4\%$ , with most samples in the  $+3$  to  $+7\%$  range [Peters *et al.*, 1978; Bebout, 1995; Kienast, 2000; Sadofsky and Bebout, 2004]. The average nitrogen isotope value of sediments off Central America is  $+5.5\%$  [Li *et al.*, 2003].

[27] In order to resolve N provenance in subduction zones, we use a three component mixing



**Figure 4.** Plot showing mixing lines between A (air), M (mantle), and S (sediment) endmembers and Costa Rica samples. Symbols as in Figure 2. Plot excludes air- and crustally contaminated samples (see text). Mixing lines from *Sano et al.* [2001]. The following endmembers were used: M has  $\delta^{15}\text{N}$  of  $-5\text{‰}$  [Marty, 1995], and  $\text{N}_2/\text{He}$  of 150 [Marty and Zimmerman, 1999]; S has  $\delta^{15}\text{N}$  of  $+5.5\text{‰}$  [Li et al., 2003], and  $\text{N}_2/\text{He}$  of 10,500 [Fischer et al., 2002]; A has  $\delta^{15}\text{N}$  of  $0\text{‰}$  and  $\text{N}_2/\text{He}$  of 148,900 [Ozima and Podosek, 2002]. Dashed lines represent proportions of N from sediment and mantle endmembers mixed with N from air, where the percent represents the relative proportion of N from sediment mixed with the mantle endmember. The majority of Costa Rica samples have received less than 50% of their nitrogen from subducted sediments, and some samples show no trace of sedimentary nitrogen.

model, following the approach of *Sano et al.* [2001]:

$$\delta^{15}\text{N}_{\text{obs}} = f_M * \delta^{15}\text{N}_{\text{mantle}} + f_S * \delta^{15}\text{N}_{\text{sed}} + f_A * \delta^{15}\text{N}_{\text{air}} \quad (3)$$

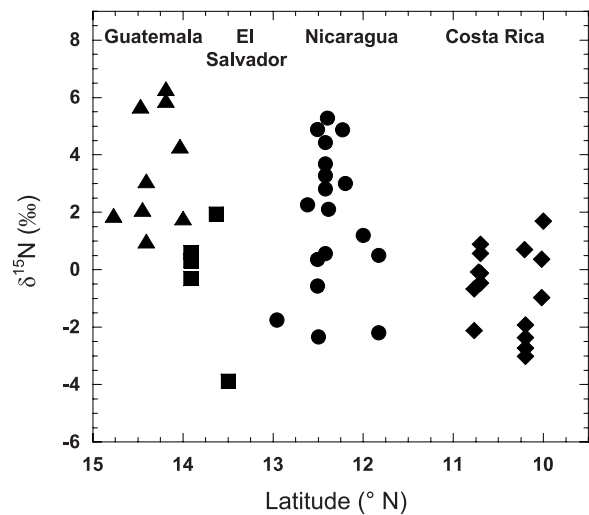
$$\frac{1}{(\text{N}_2/\text{He})_{\text{obs}}} = \frac{f_M}{(\text{N}_2/\text{He})_{\text{mantle}}} + \frac{f_S}{(\text{N}_2/\text{He})_{\text{sed}}} + \frac{f_A}{(\text{N}_2/\text{He})_{\text{air}}} \quad (4)$$

$$f_M + f_S + f_A = 1 \quad (5)$$

where obs is the observed value, and M, S, A are the contributions from mantle, marine sediments, and air, respectively (expressed as fractions,  $f$ ). End-member compositions and the calculated contribution of mantle, sediment, and air for each

sample is reported in Table 2, along with the calculated sedimentary input after removing the air contribution (%S [Fischer et al., 2002]). Figure 4 shows mixing lines between mantle, sediment, and air end-members along with the compositions of Costa Rica samples. Samples from Poás and Turrialba that fall along the air-mantle mixing curve have received no sedimentary input. Two Poás samples fall below the mantle-sediment mixing line, possibly indicating the mantle wedge below Poás is characterized by  $\text{N}_2/\text{He} < 150$  (as the mantle end-member composition was determined from a compilation of  $\text{N}_2/\text{He}$  values).

[28] Costa Rica gases display the lightest N isotope composition of CAVS gases (Figure 5), with a weighted average of  $-0.63\text{‰}$  (Table 2; the average N isotope composition was calculated by determining the average isotope compositions of sample locations with more than one value, e.g., Poás and Turrialba, then averaging the values for all sample locations). Guatemala samples range from  $-0.7$  to  $+6.3\text{‰}$ , with a weighted average of  $3.0\text{‰}$  [Fischer



**Figure 5.** Along arc variation of  $\delta^{15}\text{N}$  (measured) along CAVS. Costa Rica samples clearly have lower  $\delta^{15}\text{N}$  than the rest of the arc, suggesting a lower sedimentary N contribution. El Salvador samples also have low  $\delta^{15}\text{N}$ , but the data set is limited (only five samples). See Figure 4 caption for end member values of  $\delta^{15}\text{N}$ . Costa Rica data (diamonds) from this study and Snyder et al. [2003]; Nicaragua data (circles) from Snyder et al. [2003] and Elkins [2003]; El Salvador data (squares) from Snyder et al. [2003]; Guatemala data (triangles) from Fischer et al. [2002].

*et al.*, 2002], and Nicaragua samples range from  $-2.3$  to  $+5.3\text{‰}$  with the majority of samples having positive values [Elkins, 2003]. Moreover, the majority of Nicaragua and Guatemala samples receive  $\geq 70\%$  of their N from sediments (%S in the binary sediment-mantle mixture [Fischer *et al.*, 2002; Elkins, 2003]). This is in contrast to Costa Rica, where the average sedimentary N contribution (%S) is 37%, and some samples show no sediment signal (%S from Table 2; average %S was calculated in the same manner as average N isotope composition, except sample R1 was not included; see Figure 4 caption for explanation). Snyder *et al.* [2003] report a similar trend for N isotope compositions of CAVS geothermal wells, where Nicaraguan samples have considerably higher  $\delta^{15}\text{N}$  values than Costa Rica. El Salvador samples have an average  $\delta^{15}\text{N}$  value of  $-0.58\text{‰}$ , similar to Costa Rica, but this is largely due to one sample with a very negative value (Figure 5) [Snyder *et al.*, 2003].

[29] The generally light N isotope characteristics of Costa Rica volatiles (best exemplified by Turrialba and Poás) indicate that the major source of N is the mantle wedge, with little or no contribution to the N budget from subducted sediments. Furthermore, there is not a significant role for subducting oceanic crust in the N budget of Costa Rica. Nitrogen in metamorphic rocks from the Catalina Schist [Bebout and Fogel, 1992] and Sächsisches Erzgebirge, Germany [Haendel *et al.*, 1986] shows an inverse relationship between concentration and isotopic composition: with increasing metamorphic grade, the N concentration decreases, and the isotopic composition of residual N increases. It follows that N present in subducting oceanic crust should have a high (positive) N isotope composition. The presence of light N in volcanic gases from Costa Rica therefore suggests that N in the subducting oceanic crust is not released in this subarc region. The lack of N contribution from subducted crust in Costa Rica does not preclude a lack of N contribution further northwest along CAVS, where higher  $\delta^{15}\text{N}$  values have been reported (Guatemala and Nicaragua [Fischer *et al.*, 2002; Elkins, 2003]). However, negligible N contribution from oceanic crust in Central America has also been argued by Snyder *et al.* [2003]

**Table 3.** Volatile Fluxes of Poás Volcano and the Costa Rican Segment of CAVS<sup>a</sup>

CO <sub>2</sub> /S <sub>t</sub> Ratio	Poás	Costa Rica	Costa Rica
	5.9	5.9	2.7
CO <sub>2</sub>	2.79*10 <sup>8</sup>	6.42*10 <sup>9</sup>	2.94*10 <sup>9</sup>
S <sub>t</sub>	4.73*10 <sup>7</sup>	1.09*10 <sup>9</sup>	4.99*10 <sup>8</sup>
SO <sub>2</sub>	4.33*10 <sup>7</sup>	9.99*10 <sup>8</sup>	4.57*10 <sup>8</sup>
H <sub>2</sub> S	4.02*10 <sup>6</sup>	9.26*10 <sup>7</sup>	4.24*10 <sup>7</sup>
HCl	5.75*10 <sup>6</sup>	1.33*10 <sup>8</sup>	6.07*10 <sup>7</sup>
He	2.54*10 <sup>3</sup>	5.86*10 <sup>4</sup>	2.68*10 <sup>4</sup>
H <sub>2</sub>	7.64*10 <sup>4</sup>	1.76*10 <sup>6</sup>	8.06*10 <sup>5</sup>
Ar	8.58*10 <sup>3</sup>	1.98*10 <sup>5</sup>	9.05*10 <sup>4</sup>
N <sub>2</sub>	6.82*10 <sup>5</sup>	1.57*10 <sup>7</sup>	7.19*10 <sup>6</sup>
N <sub>2-exc</sub>	3.39*10 <sup>5</sup>	7.81*10 <sup>6</sup>	3.57*10 <sup>6</sup>
H <sub>2</sub> O	2.92*10 <sup>10</sup>	6.73*10 <sup>11</sup>	3.08*10 <sup>11</sup>

<sup>a</sup> Volatile fluxes calculated for Poás and Costa Rica, in mol/yr, using chemistry ( $X_i/\text{CO}_2$ ) of sample P5 (Poás volcano). Poás fluxes calculated using a SO<sub>2</sub> flux of  $4.73*10^7$  mol/yr. Volatile fluxes for Costa Rica calculated a SO<sub>2</sub> flux of  $1.09*10^9$  mol/yr.

using  $^3\text{He}/^4\text{He}$ ,  $\text{N}_2/{}^3\text{He}$ , and  $\delta^{15}\text{N}$  analyses of geothermal gases.

[30] Irazú and Turrialba volcanoes present a unique case in which to examine the progression of N systematics during subduction. The volcanoes are in close proximity (Turrialba is located  $\sim 10$  km behind Irazú, relative to the strike of the trench). Turrialba potentially may be utilizing the package of subducted sediments that Irazú has already tapped. U/La is a sensitive tracer of recycled hemipelagic sediments in CAVS [Patino *et al.*, 2000; Plank *et al.*, 2002]. Higher U/La of Irazú volcanics (average 0.07 [Carr *et al.*, 2003]) compared to Turrialba volcanics (0.04 [Reagan and Gill, 1989]) support a diminished hemipelagic sediment contribution to Turrialba. Irazú has higher N<sub>2</sub>/He and  $\delta^{15}\text{N}$  than Turrialba, consistent with the U/La data and the notion that N primarily resides in the hemipelagic sediments [Sadofsky and Bebout, 2004; Li *et al.*, 2003; Fischer *et al.*, 2002] and that the sediments contribute progressively less to magma genesis with increasing slab depth. The presence of sedimentary N in Turrialba also indicates that the N budget is not completely exhausted at subarc depths.

## 5.2. Volatile Flux From Costa Rica

[31] The total flux of various volatiles from the Costa Rica segment of CAVS can be estimated



using the measured SO<sub>2</sub> fluxes from Poás and Arenal; we use Poás to illustrate the approach. Because both the volatile chemistry and SO<sub>2</sub> flux of Poás volcano are known, the flux of each gas species can be calculated using:

$$f_i = X_i/X_{\text{SO}_2} * f_{\text{SO}_2} \quad (6)$$

where  $f_i$  is the flux of species  $i$ ,  $X_i$  is the concentration of species  $i$  in the gas sample,  $X_{\text{SO}_2}$  is the concentration of SO<sub>2</sub> in the gas sample, and  $f_{\text{SO}_2}$  is SO<sub>2</sub> flux. H<sub>2</sub>S is likely oxidized to SO<sub>2</sub> during interaction with air, so the value of  $X_{\text{SO}_2}$  used in the calculation is that of  $X_{\text{S}_t}$ . Table 3 lists the volatile fluxes calculated for Poás volcano using the SO<sub>2</sub> flux of 1.30\*10<sup>5</sup> mol/day. Sample P5 is the gas sample used to determine  $X_i/\text{SO}_2$  values because it was collected three days prior to COSPEC measurements.

[32] We estimate a volatile flux for Costa Rica using the method of *Brantley and Koepenick* [1995], noting that *Hilton et al.* [2002] successfully applied this method to estimate volatile fluxes of individual arcs. Assuming flux distribution follows a power law, the following function describes the number of volcanoes,  $N$ , with an emission rate  $\geq f$ :

$$N = af^{-c}, \quad (7)$$

where  $a$  and  $c$  are constants, and  $c < 1$  for the equation to be valid. A solution for the function by *Marrett and Allmendinger* [1992] can be used to estimate total flux ( $f_{\text{tot}}$ ):

$$f_{\text{tot}} = f_1 + f_2 + f_3 + \dots + f_N \left[ \left( \frac{c}{1-c} \right) (N+1) \left( \frac{N}{(N+1)} \right)^{1/c} \right] \quad (8)$$

where  $f_1$  is the largest flux,  $f_2$  is the second largest flux, and  $f_N$  refers to the  $N$ th largest flux. This solution accounts for volcanoes emitting smaller fluxes that are not measured. A  $c$  value for Central America (0.46) was calculated by plotting log SO<sub>2</sub> flux of twelve Central American volcanoes against log volcano number ( $N$ ). Fluxes used to calculate  $c$  are from *Andres and Kasgnoc* [1998], with the exception that our flux measurements were substituted for Arenal and Poás. Fluxes of Arenal and

Poás from this study were then used to obtain  $f_{\text{tot}}$ . The SO<sub>2</sub> flux for the Costa Rica volcanoes is 1.91\*10<sup>5</sup> kg/day (1.09\*10<sup>9</sup> mol/yr). This estimate, only slightly higher than the sum of SO<sub>2</sub> fluxes from Arenal and Poás (1.88\*10<sup>5</sup> kg/day, or 1.07\*10<sup>9</sup> mol/yr), seems reasonable given that there are no visible plumes in Costa Rica besides those at Arenal and Poás.

[33] Because of the observed variations in the chemistry of discharging Costa Rica gases and the resulting consequences for volatile fluxes (calculated using SO<sub>2</sub> emissions and gas ratios), it is important to evaluate which gas compositions are most representative of Costa Rica. The most representative magmatic volatile compositions are obtained from high temperature (>400°C) volcanic fumaroles where processes such as sulfur precipitation and partitioning into a hydrothermal system to form H<sub>2</sub>SO<sub>4</sub> do not occur [*Giggenbach and Matsuo*, 1991; *Giggenbach*, 1996]. In arc settings worldwide, high temperature volcanic gases have CO<sub>2</sub>/S<sub>t</sub> of 0.4–5, independent of magma composition [*Shinohara et al.*, 1993; *Symonds et al.*, 1994; *Giggenbach*, 1996; *Taran et al.*, 1995; *Fischer et al.*, 1998]. It follows that the CO<sub>2</sub>/S<sub>t</sub> of Poás (5.9) is the most representative of the mantle source region and most appropriate to obtain the CO<sub>2</sub> flux from the mantle. For comparison, fluxes are also calculated using average CO<sub>2</sub>/S<sub>t</sub> of CAVS (2.7 [*Hilton et al.*, 2002]). We use these ratios in Equation (6) to calculate CO<sub>2</sub> fluxes of Costa Rica, resulting in fluxes of 6.42\*10<sup>9</sup> (CO<sub>2</sub>/S<sub>t</sub> = 5.9) and 2.94\*10<sup>9</sup> (CO<sub>2</sub>/S<sub>t</sub> = 2.7) mol/yr.

[34] Next, we next compare our values to those in the literature. Extrapolating our CO<sub>2</sub> flux to CAVS by scaling to arc trench lengths yields CO<sub>2</sub> fluxes of 3.00\*10<sup>10</sup> (CO<sub>2</sub>/S<sub>t</sub> = 5.9) and 1.37\*10<sup>10</sup> (CO<sub>2</sub>/S<sub>t</sub> = 2.7) mol/yr (arc trench lengths are 310 km and 1450 km for Costa Rica and Central America, respectively [*von Huene and Scholl*, 1991; *Protti et al.*, 1995]). *Hilton et al.* [2002] report a CO<sub>2</sub> flux for CAVS of 5.8\*10<sup>10</sup> mol/yr (calculated using COSPEC SO<sub>2</sub> flux measurements, CO<sub>2</sub>/S<sub>t</sub> = 2.7 (CAVS average CO<sub>2</sub>/S<sub>t</sub>), and the estimation technique of *Brantley and Koepenick* [1995]. *Shaw et al.* [2003] use the average CO<sub>2</sub>/<sup>3</sup>He of Costa Rica and Nicaragua (2.3\*10<sup>10</sup>) and the CAVS <sup>3</sup>He flux



of *Hilton et al.* [2002], scaled to the trench length of Costa Rica, to calculate a CAVS CO<sub>2</sub> flux of  $7.10 \cdot 10^{10}$  mol/yr. The CO<sub>2</sub> fluxes are very similar (within a factor of 2–3).

[35] We note that the SO<sub>2</sub> flux of Poás volcano ( $8.30 \cdot 10^3$  kg/day) was significantly lower in March 2001 than it has been in the past (e.g., 1981–1983). *Andres and Kasgnoc* [1998] list time-averaged fluxes of  $5.0 \cdot 10^5$  and  $1.0 \cdot 10^5$  kg/day ( $7.81 \cdot 10^6$  and  $1.56 \cdot 10^6$  mol/day) for Poás and Arenal volcanoes, respectively. Still, low sulfur emissions continue to characterize Poás, as a SO<sub>2</sub> flux of  $2.90 \cdot 10^4 \pm 9.0 \cdot 10^3$  kg/day ( $4.53 \cdot 10^5 \pm 1.41 \cdot 10^5$  mol/day) was measured in March 2003 (Marie Edmonds, personal communication, 2003). The low flux of Poás may be related to its decreased activity. Higher fluxes previously reported were measured during a time of increased volcanic activity in the 1980s, as characterized by phreatic eruptions, low frequency seismic events, abundant fumaroles, and fumarole temperatures up to 1020°C [*Rowe et al.*, 1992]. It is quite common for volcanoes to emit significantly higher gas fluxes during periods of increased volcanic activity [e.g., *Casadevall et al.*, 1994; *Zapata et al.*, 1997]. However, as low levels of activity are expected to dominate the life cycle of a particular volcano, the lower fluxes maybe more representative of the long-term average of a volcano's output. Table 3 shows fluxes of remaining volatiles, calculated using  $X_i/\text{CO}_2$  and CO<sub>2</sub> fluxes above.

### 5.3. Costa Rica's Volatile Contribution to CAVS and Mass Balance

[36] The sediment column does not vary greatly along strike of CAVS [*Aubouin and Shipboard Scientific Party*, 1982; *Kimura and Shipboard Scientific Party*, 1997], thus input to the trench from subducting sediments and oceanic crust can be considered constant. Costa Rica makes up 21% of the length of the arc, therefore Costa Rica should contribute this proportion to the volatile output. Volatile outputs of CO<sub>2</sub> and N<sub>2-exc</sub> for CAVS are  $5.75 \cdot 10^{10}$  and  $2.94 \cdot 10^8$  mol/yr, respectively [*Hilton et al.*, 2002]. The percentages of Costa Rica's contribution to N<sub>2-exc</sub> and CO<sub>2</sub> CAVS

volatile fluxes are 2.7% and 11.2%, respectively, for a CO<sub>2</sub>/S<sub>t</sub> of 5.9, and 1.2% and 5.1%, respectively, for a CO<sub>2</sub>/S<sub>t</sub> of 2.7. In each case, Costa Rica contributes significantly less than 21% (the proportion of CAVS represented by Costa Rica). Possibilities for this discrepancy are discussed below.

[37] The ratio of N released in arc gases to N being subducted in oceanic crust and sediments is a key parameter in assessing N mass balance. If input includes the N content of subducting sediments (0.01 wt.%) and oceanic crustal basement (0.001 wt.% [e.g., *Hilton et al.*, 2002]) then the output/input ratio is substantially less than unity for Central America (0.14). However, subducted oceanic crust is an unlikely contributor of N. If N resides only in subducting hemipelagic sediments, as suggested by *Fischer et al.* [2002] based upon the  $\delta^{15}\text{N-N}_2/\text{He}$  systematics, then output/input approaches unity [*Fischer et al.*, 2002].

[38] We examine recycling efficiency, defined as output/input, of N and C subduction in Costa Rica. Nitrogen recycling efficiency was evaluated using three inputs. The first input is based on an estimated N concentration of 0.01 wt.% in subducted sediments (based in part on mass balance considerations of *Bebout* [1995]) and revised to reflect only N input from subducted hemipelagic sediments [*Fischer et al.*, 2002]. The second N input is based on N concentrations recently measured in hemipelagic sediments from DSDP Leg 170 drill cores [*Li et al.*, 2003; L. Li, personal communication, 2003], and considers the carbonate section as containing 0 ppm N. While the lower pelagic carbonate section of the incoming sediments could contain appreciable N due to its large volume, the N contribution will be minor in comparison with that from the hemipelagic sediments; low N concentrations (<30 ppm) in carbonate-rich and siliceous sediments from the Izu-Bonin margin (Site 1149) were reported by *Sadofsky and Bebout* [2004]. To account for the possible contribution of N from by carbonate sediments, the third input considers the lower, chalk/nanofossil ooze section as containing 30 ppm N, in addition to the N input of the hemipelagic sediments from *Li et al.* [2003]. This section mostly contains >70 wt.% calcite

**Table 4.** Recycling Efficiency (Output/Input) of Nitrogen and Carbon in Costa Rica

Input Parameters	N <sub>2</sub> Efficiency 1	N <sub>2</sub> Efficiency 2	N <sub>2</sub> Efficiency 3	CO <sub>2</sub> Efficiency <sup>a</sup>
C/S = 5.9 <sup>a</sup>	0.06	0.03	0.03	0.08
C/S = 2.7 <sup>a</sup>	0.03	0.01	0.01	0.04
Input, hemipelagic seds (10 <sup>7</sup> mol/yr)	4.92 <sup>b</sup>	9.96 <sup>c</sup>	9.96 <sup>c</sup>	–
Input, carbonate seds (10 <sup>7</sup> mol/yr)	0	0	0.564 <sup>d</sup>	7810
Total input (hemipelagic + carbonate sediments; 10 <sup>7</sup> mol/yr)	4.92	9.96	10.5	7810

<sup>a</sup> Carbon and nitrogen output from Table 3; N<sub>2-exc</sub> used as N<sub>2</sub> output. N fluxes from Table 3 were multiplied by 0.37 (average %S) to reflect only sedimentary output: for C/S = 5.9, N<sub>2</sub> output = 2.89\*10<sup>6</sup> mol/yr; CO<sub>2</sub> output = 6.42\*10<sup>9</sup>. For C/S = 2.7, N<sub>2</sub> output = 1.32\*10<sup>6</sup> mol/yr; CO<sub>2</sub> output = 2.94\*10<sup>9</sup>.

<sup>b</sup> Fischer *et al.* [2002].

<sup>c</sup> Li *et al.* [2003], L. Li (personal communication, 2003).

<sup>d</sup> N<sub>2</sub> input from carbonate sediments calculated assuming a 30 ppm N concentration [Sadofsky and Bebout, 2004], 250 m thick carbonate section [Aubouin and Shipboard Scientific Party, 1982; Kimura and Shipboard Scientific Party, 1997], average dry bulk density of 0.79 g/cc [Kimura and Shipboard Scientific Party, 1997], and a convergence rate of 86 mm/yr [DeMets *et al.*, 1990; Protti *et al.*, 1995].

[Kimura and Shipboard Scientific Party, 1997], but minor intermixing of more clay- and organic-rich material could elevate the whole-sediment N contents. Carbon input (from subducted organic sediments, carbonates, and oceanic crust) is from Hilton *et al.* [2002]. Nitrogen and carbon fluxes from Table 3 are used as output. However, N output fluxes include both sedimentary and mantle N. In order to correctly assess mass balance of subducted material, N<sub>2-exc</sub> fluxes were revised to reflect only sedimentary N. The average %S of Costa Rica gases is 37, thus the N output fluxes were multiplied by 0.37 for the calculations of Table 4.

[39] Nitrogen and carbon recycling efficiencies are significantly less than unity (0.01–0.08; Table 4). This conclusion is not surprising given Costa Rica's low N and C contribution to the CAVS volatile output. Taking into account the possible N contribution of carbonate sediments has a minor effect on the N recycling efficiency. The low efficiencies imply that more N and C are being subducted than released at the volcanic front in Costa Rica. This is in contrast to the rest of the arc where the N cycle is closer to being balanced [Fischer *et al.*, 2002]. The discrepancy arises because this work uses a total N<sub>2-exc</sub> flux of (3.5–7.8) × 10<sup>6</sup> mol/yr as determined for Costa Rica. As discussed above, the Costa Rica arc section is characterized by low sedimentary contribution to the N output (average %S = 37%) and a low volatile flux of 1.91\*10<sup>5</sup> kg/day (2.98\*10<sup>6</sup> mol/day) SO<sub>2</sub>, compared to the rest

of the arc (e.g., Masaya, Nicaragua emits 1.80\*10<sup>6</sup> kg/day (2.81\*10<sup>7</sup> mol/day) SO<sub>2</sub> [Burton *et al.*, 2000]). The Costa Rica N<sub>2-exc</sub> flux, when scaled to CAVS, would give a total arc output flux of 1.3 × 10<sup>7</sup> mol/yr. This N<sub>2-exc</sub> flux is an order of magnitude lower than the 2.9 × 10<sup>8</sup> mol/yr of Fischer *et al.* [2002], calculated using SO<sub>2</sub> fluxes and SO<sub>2</sub>/N<sub>2</sub> of the entire CAVS from Hilton *et al.* [2002]. On the basis of the work presented here, Costa Rica's low volatile output and low N<sub>2</sub>/He result in a comparatively low N<sub>2</sub> flux from this section of the arc. Because the N input does not vary along the strike of CAVS, the N (and C) budgets are not balanced. An additional factor for the N imbalance is that the N flux from Poás reported here is considerably lower than any previously reported flux for the volcano. If the flux of Poás increases to values previously reported, recycling efficiency will increase, as will Costa Rica's volatile contribution to CAVS. Increasing the volatile flux of Poás by a factor of ~50 would approximately balance the N budget.

[40] If the low efficiency of recycling of N<sub>2</sub> and CO<sub>2</sub> and low contribution to the total volatile flux of Costa Rica to CAVS is correct, then there are several possible explanations. First of all, the Costa Rican volcanoes were not very active during the sampling interval; more frequent eruptions would have released more volatiles in the given time span. Next, if N primarily resides in the hemipelagic sediments [Sadofsky and Bebout, 2004; Fischer *et al.*, 2002], then under-

plating of the uppermost section of the sediment column [Shipley *et al.*, 1990] may play a role in preventing N from reaching the Costa Rican subarc. Kerrick and Connolly [2001] suggest forearc devolatilization of clay-rich marls in arcs coupled with warm thermal regimes is partly responsible for low CO<sub>2</sub> fluxes from arcs. Similarly, low N emissions in Costa Rica may arise from the shallow slab dip in this region, consistent with a warmer thermal regime [e.g., Chen *et al.*, 2001], resulting in devolatilization and loss of N in the forearc region [see also Fryer *et al.*, 1985; Brown, 1990, Busigny *et al.*, 2003]. However, the relationship between slab dip and thermal structure is currently unresolved [e.g., Furukawa, 1993; Kincaid and Sacks, 1997; Chen *et al.*, 2001]. Shallower slab dip in this region may result in fluid release from metamorphic reactions occurring over a greater extent during subduction, thus limiting fluid availability per unit mantle and leading to decreased mobilization of fluid-mobile elements [Feigenson and Carr, 1986; Carr *et al.*, 1990; Rupke *et al.*, 2002]. Limited fluid availability has been suggested to explain decreased decarbonation in shallowly dipping subduction zones [Kerrick and Connolly, 2001] and may limit N release as well. Nitrogen may also be bound in a mineral phase and subducted beyond the subarc, consistent with high N contents in metamorphic microdiamonds from the Kokchetav massif, Kazakhstan [Cartigny *et al.*, 2001; Busigny *et al.*, 2003].

## 6. Conclusions

[41] In general, Costa Rica arc volatiles do not display typical arc-type chemistry, having N<sub>2</sub>/He lower than the range reported at other arc volcanoes. Poás and Turrialba gases display the lowest N<sub>2</sub>/He, indicative of minor or negligible modification by slab input. Samples from most locations indicate influence by shallow hydrothermal processes, resulting in CO<sub>2</sub>/S<sub>t</sub> > 10, with the exception of Poás volcano. Costa Rica displays a lower average N isotope composition than Nicaragua or Guatemala, with Poás having δ<sup>15</sup>N values similar to the mantle (MORB) end-member. We apply the flux extrapolation method of

Brantley and Koepenick [1995] to calculate a SO<sub>2</sub> flux for the Costa Rican segment of CAVS. The flux estimate is considerably lower than previous estimates due to the low flux measured at Poás volcano (>50 times less than published values). The N<sub>2</sub>/He, CO<sub>2</sub>/S<sub>t</sub>, and N isotopes indicate volcanic gases at Poás are the most representative of the underlying magma source, thus we use its chemistry to calculate remaining volatile fluxes for the Costa Rican segment. Assuming subducted oceanic crust and carbonate sediments do not contribute to the N budget, significantly more N is subducted than released at the volcanic front in Costa Rica. If this low output is correct, then possibilities for poor N recycling efficiency include sediment underplating, forearc devolatilization, limited fluid availability in the subarc region, and subduction of N past the zone of magma generation.

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