Earth and Planetary Science Letters 407 (2014) 134–147

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Gas measurements from the Costa Rica–Nicaragua volcanic segment suggest possible along-arc variations in volcanic gas chemistry

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ARTICLE INFO

Article history:
Received 10 May 2014
Received in revised form 23 September 2014
Accepted 23 September 2014
Available online 13 October 2014
Editor: B. Marty

Keywords:
volcanic gases
CO_2 flux
arc volcanism
CAVA
Costa Rica
Nicaragua

ABSTRACT

Obtaining accurate estimates of the CO_2 output from arc volcanism requires a precise understanding of the potential along-arc variations in volcanic gas chemistry, and ultimately of the magmatic gas signature of each individual arc segment. In an attempt to more fully constrain the magmatic gas signature of the Central America Volcanic Arc (CAVA), we present here the results of a volcanic gas survey performed during March and April 2013 at five degassing volcanoes within the Costa Rica–Nicaragua volcanic segment (CNVS). Observations of the volcanic gas plume made with a multicomponent gas analyzer system (Multi-GAS) have allowed characterization of the CO_2/SO_2-ratio signature of the plumes at Poás (0.30 ± 0.06, mean $\pm$ SD), Rincón de la Vieja (27.0 ± 15.3), and Turrialba (2.2 ± 0.8) in Costa Rica, and at Telica (3.0 ± 0.9) and San Cristóbal (4.2 ± 1.3) in Nicaragua (all ratios on molar basis). By scaling these plume compositions to simultaneously measured SO_2 fluxes, we estimate that the CO_2 outputs at CNVS volcanoes range from low (25.5 ± 11.0 tons/day at Poás) to moderate (918 to 1270 tons/day at Turrialba). These results add a new information to the still fragmentary volcanic CO_2 output data set, and allow estimating the total CO_2 output from the CNVS at 2835 ± 1364 tons/day. Our novel results, with previously available information about gas emissions in Central America, are suggestive of distinct volcanic gas CO_2/S_T ($= SO_2 + H_2S$)-ratio signature for magmatic volatiles in Nicaragua ($\sim$3) relative to Costa Rica ($\sim$0.5–1.0). We also provide additional evidence for the earlier theory relating the CO_2-richer signature of Nicaragua volcanism to increased contributions from slab-derived fluids, relative to more-MORB-like volcanism in Costa Rica. The sizeable along-arc variations in magmatic gas chemistry that the present study has suggested indicate that additional gas observations are urgently needed to more-precisely confine the volcanic CO_2 from the CAVA, and from global arc volcanism.

1. Introduction

Characterizing the volcanic gas outputs along active volcanic-arc regions is crucial to quantifying the recycling of volatiles at subducting slabs and its consequences for arc magmatism (Hilton et al., 2002). The long-term (geological) volcanic-arc CO_2 budget (Wallace, 2005) is particularly critical to better constraining the relative C contributions from the slab, the mantle wedge, and the crust, and for predicting how arc degassing influences the atmospheric CO_2 budget and climate models (Berner and Lasaga, 1989).

In recent years a mass balance approach has been used to extensively investigate exchanges of volatiles at subduction zones (Fischer et al., 2002; Hilton et al., 2002). However, the global subaerial volcanic CO_2 flux, which is dominated by arc volcanism (Marty and Tolstikhin, 1998), remains poorly constrained, with current estimates ranging widely, from 65 to 540 Mt/yr (see review by Burton et al., 2013). CO_2 budgets for individual arc segments are also generally poorly understood (Hilton et al., 2002). In addition to estimates of the SO_2 output being incomplete and/or inaccurate, a major issue in deriving the CO_2 outputs from individual arcs is assigning a "representative" CO_2/SO_2 ratio to them. This remains problematic due to the limited data set of high-temperature volcanic gases that is available (Fischer, 2008), and the potentially

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http://dx.doi.org/10.1016/j.epsl.2014.09.041
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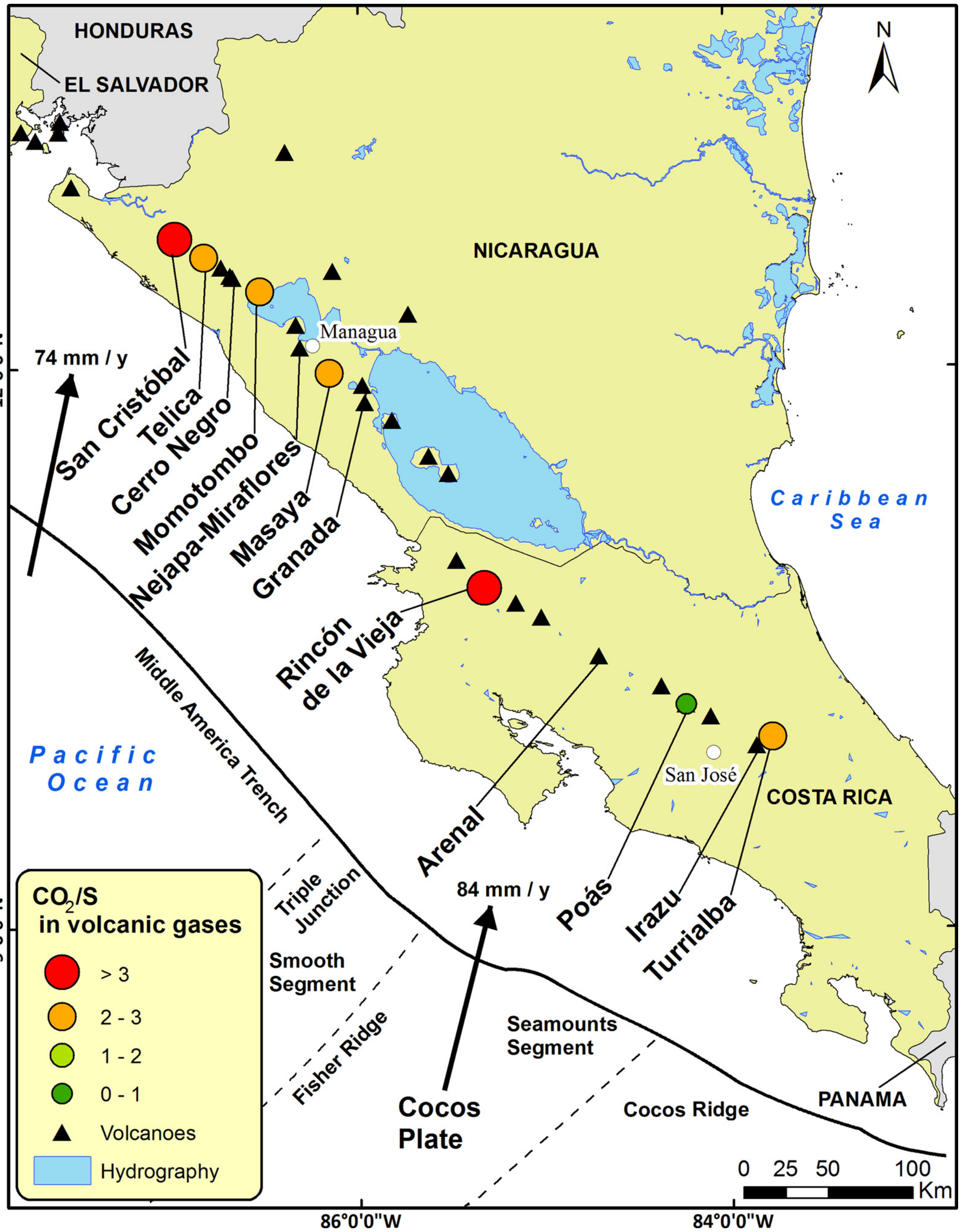

Fig. 1. Map of the subduction zone in Nicaragua and Costa Rica. Black arrows indicate the direction of motion of the Cocos Plate and the convergence velocities relative to the Caribbean Plate (in millimeters per year) after DeMets (2001). Plate segments and trench structures are interpreted from the bathymetry imagery in von Huene et al. (2000). The volcanic gas molar CO_2/S_T ratios indicated in the figure are from the present study except for Momotombo (Menyailov et al., 1986) and Masaya (Martin et al., 2010). CVS and NVS identify the Costa Rica and Nicaragua volcanic segments, respectively.

large variations in gas chemistry within a given arc segment, between different segments, and at individual volcanoes.

Herein we present experimental evidence for sizeable variations in the gas composition along the Costa Rica–Nicaragua volcanic segment (CNVS) of the CAVA (Fig. 1). Previous work in the region (Shaw et al., 2003; Zimmer et al., 2004; Elkins et al., 2006; Fischer et al., 2007) has concentrated on the chemical and isotopic systematics of poorly reactive (CO_2) or inert (N_2 and He) gases, with the majority of samples being low temperature. We concentrate here instead on determining the CO_2/SO_2 and H_2O/CO_2 ratios in the large, high-temperature emissions that generally dominate – and are therefore more appropriate to confine – the volcanic-arc CO_2 output (Shinohara, 2013). The CO_2/SO_2 signature of CAVA volcanism has been assigned constant values in previous CO_2 regional inventories (Hilton et al., 2002; Mather et al., 2006; Fischer, 2008), whereas the structural and magmatological complexities of the arc (Carr et al., 2003) make the existence of substantial along-arc variations highly plausible.

The results reported herein were obtained in the course of a gas survey conducted during March and April 2013 with the aim of characterizing the chemistry of the volcanic gas plume at five strong degassing volcanoes: Turrialba, Poás, and Rincón de la Vieja in Costa Rica, and San Cristóbal and Telica in Nicaragua. We combine our newly acquired data set with previous gas information in the region (i) to better confine the CO_2/SO_2 signature(s) of this arc segment, (ii) to derive a volcanic CO_2 budget for the region, and (iii) to infer new constraints on the (mantle vs. slab) origin of arc CO_2.

2. The Costa Rica–Nicaragua volcanic arc segment

Costa Rica and Nicaragua host an exceptionally well-studied arc segment (Fig. 1), which forms part of the CAVA (Fig. 1). The well-documented structural (Protti et al., 1995; MacKenzie et al., 2008) and geochemical (Carr, 1984; Carr et al., 1990, 2003; Patino et al., 2000; Sadofsky et al., 2008) variations that occur along the CNVS make it particularly suitable for investigating along-arc changes in volcanic gas chemistry. The entire arc segment is related to subduction (at a convergence rate of ∼90 mm/yr; Protti et al., 1995) of the Cocos Plate beneath the Caribbean Plate (Fig. 1). However, the subduction angle of the slab is far steeper in Nicaragua (up to 84°) than in central Costa Rica (60°), which reflects different ages and thermal regimes of subducted oceanic crust (Protti et al., 1995). The steep subduction in Nicaragua and the extensive serpentinization of the subducted mantle are thought to allow a large influx of recycled slab fluids and a high degree of partial melting of a relatively small-volume mantle wedge (Carr et al., 1990; Abers et al., 2003). This would ultimately result in the influence of the slab on magma petrogenesis being larger in Nicaragua (e.g., the highest Ba/La, B/La, and $^{10}Be/^{9}Be$ ratios in CAVA lavas; Carr et al., 1990). In contrast, relatively low subduction fluxes of hemipelagic sediments and a dominant contribution of the mantle wedge to petrogenesis have been postulated for Costa Rica (Eiler et al., 2005). Underplating of hemipelagic sediment to the over-riding Caribbean plate has been invoked as one of the casual factors (Leeman et al., 1994).

A larger contribution of sedimentary slab fluids in Nicaragua relative to Costa Rica is also supported by along-arc geochemical variations in the compositions of volatiles (see review by Fischer et al., 2007). These studies have for instance found that the ratio of slab-derived C (from both limestones and organic sediments) to mantle-derived C is substantially greater in Nicaragua than in Costa Rica (Shaw et al., 2003; De Leeuw et al., 2007). The gases sampled in these studies were dominated by relatively low T emissions, thus, investigating the existence of such trends in volatiles also in high-temperature magmatic gases was one of the central objectives of the present study.

3. Methodology

We investigated the volcanic gas plumes of Turrialba, Poás, and Rincón de la Vieja (all in Costa Rica) and of San Cristóbal and Telica (both in Nicaragua) (Fig. 1) by using a custom-made multicomponent gas analyzer system (called Multi-GAS henceforth). The Multi-GAS, whose first volcano applications emerged in the mid-2000s (Aiuppa et al., 2005; Shinohara, 2005), is a compact unit constructed by assembling different commercial Infra-Red (for CO_2 and H_2O) and electrochemical (for SO_2 and H_2S) gas sensors. The same sensor assemblage as in Aiuppa et al. (2009, 2010, 2012) was used in the present study. We employed two distinct types of Multi-GAS. At Turrialba, Poás, San Cristóbal, and Telica, we temporarily deployed a fixed, fully autonomous version of the Multi-GAS, similar to the systems used in other permanent networks (e.g., Stromboli; Aiuppa et al., 2009). The fixed Multi-GAS, powered by a 12-V lead-acid battery connected to a photovoltaic module, ran unattended at Turrialba from March 12 to March 19, 2013; at Telica from March 22 to April 8, 2013; at San Cristóbal from April 11 to 16, 2013; and at Poás during April 16–18, 2013. The Turrialba and Telica data have been presented in Conde et al. (in press). In that paper, we focused on a comparison between FTIR and Multi-GAS results, and on the implications of combined DOAS–Multi-GAS data sets to quantification of the CO_2 output. We here discuss the observations of Conde et al. (in press) in a broader context of volcanic gas origin and variation along CAVA. At all volcanoes the fixed Multi-GAS was deployed at a location within the active crater(s) area, from tens to a few hundreds of meters from the main degassing vent(s), which ensured frequent fumigation by the plume (Fig. 2). The instrument was programmed to measure the concentrations of various gases (H_2O, CO_2, SO_2, and H_2S) in the plume at a sampling rate of 0.1 Hz, in cycles lasting for 30 min (four to eight daily cycles were performed, depending on power availability). Given the difficulty of accessing Rincón de la Vieja, a lighter (<2 kg) portable Multi-GAS (powered by an internal lithium battery) was used for a rapid survey performed on April 8, 2013, at which about 3 h of Multi-GAS data were acquired at 0.5 Hz. The same unit was used to repeat additional measurements at Turrialba during April 2–4, 2013. Table 1 summarizes Multi-GAS results.

The SO_2 output was measured at each volcano except Rincón de la Vieja (Table 2). SO_2 column columns were retrieved by applying differential optical absorption spectroscopy (DOAS) to spectra which source of radiation was ultraviolet (UV)-scattered sunlight (Platt and Stutz, 2008). At San Cristóbal and Turrialba, we used UV scanning spectrometers part of the NOVAC network (Galle et al., 2010); while at Telica a temporal installation of NOVAC instruments was set up (Conde et al., in press). At Poás the SO_2 flux was measured by traversing underneath the plume with a vertically pointed UV spectrometer.

4. Volcanic activity

The five volcanoes were all degassing strongly to moderately during our observations, but no eruptive activity was observed. Our observations are therefore representative of periods of "regular" degassing activity for all the volcanoes studied. Turrialba (Fig. 2a) was degassing intensively in March and April 2013 from two active vents inside the west crater (2010 vent and 2012 vent), which formed during the January 5, 2010 and January 12, 2012 vent-opening eruptions, respectively (OVSICORI-UNA, 2012). The vent temperatures ranged from 400 to 590 °C (at Vent 2010) up to 800 °C (at Vent 2012) (Table 1; data from OVSICORI-UNA, 2013). The 2011 vent (Fig. 2) was degassing more moderately during our measurements. Poás (Fig. 2b) was showing intense degassing in mid-April 2013 from a fumarole field between the shore of the crater lake and the dome (on the top of which the Multi-GAS was installed; Fig. 2b). The fumaroles of the dome, which had started a new heating cycle in early 2013, had a temperature of ∼500 °C on April 16 (OVSICORI-UNA, 2013), and a total SO_2 output of 124 ± 33 tons was measured on the same day (average and SD of 8 walking traverses under the fumarolic plume). Given the high temperature of the dome during our sampling, and our measurement location right ontop of the dome itself, we can rule out any major influence from the lake. During our visit on April 6, 2013, Rincón de la Vieja (Fig. 2c) hosted a hyperacidic (pH ∼ 0.1), warm (∼36 °C), intracrateric volcanic lake, and several fumaroles at ∼130 °C (temperature measured with IR camera). Both types of emission contributed to the bulk plume, which was measured by the Multi-GAS from the northern, outer rim of the summit crater. Telica (Fig. 2d) is a restless volcano in western Nicaragua, where persistent degassing is frequently interrupted by small explosions (VEI 1–3). Few studies have investigated plume gases at Telica (Witt et al., 2008; Conde et al., in press). The volcano has exhibited passive degassing during 2011–2014 at an average rate of 140 ± 100 tons/day SO_2 (Geirsson et al., 2014). Incandescence was observed during our survey in a major vent (with a peak temperature of 507 °C) located ∼120 m deep inside the crater (INETER, 2013). San Cristóbal (Fig. 2e) has recently exhibited irregular degassing in response to eruptive activity (2 eruptive events/year on average during the past few years; INETER, 2013). The SO_2 flux (measured by NOVAC instruments) ranged from 2000 to 4000 tons/day at the time of the VEI 2 explosion on December 2, 2012. Immediately after this event

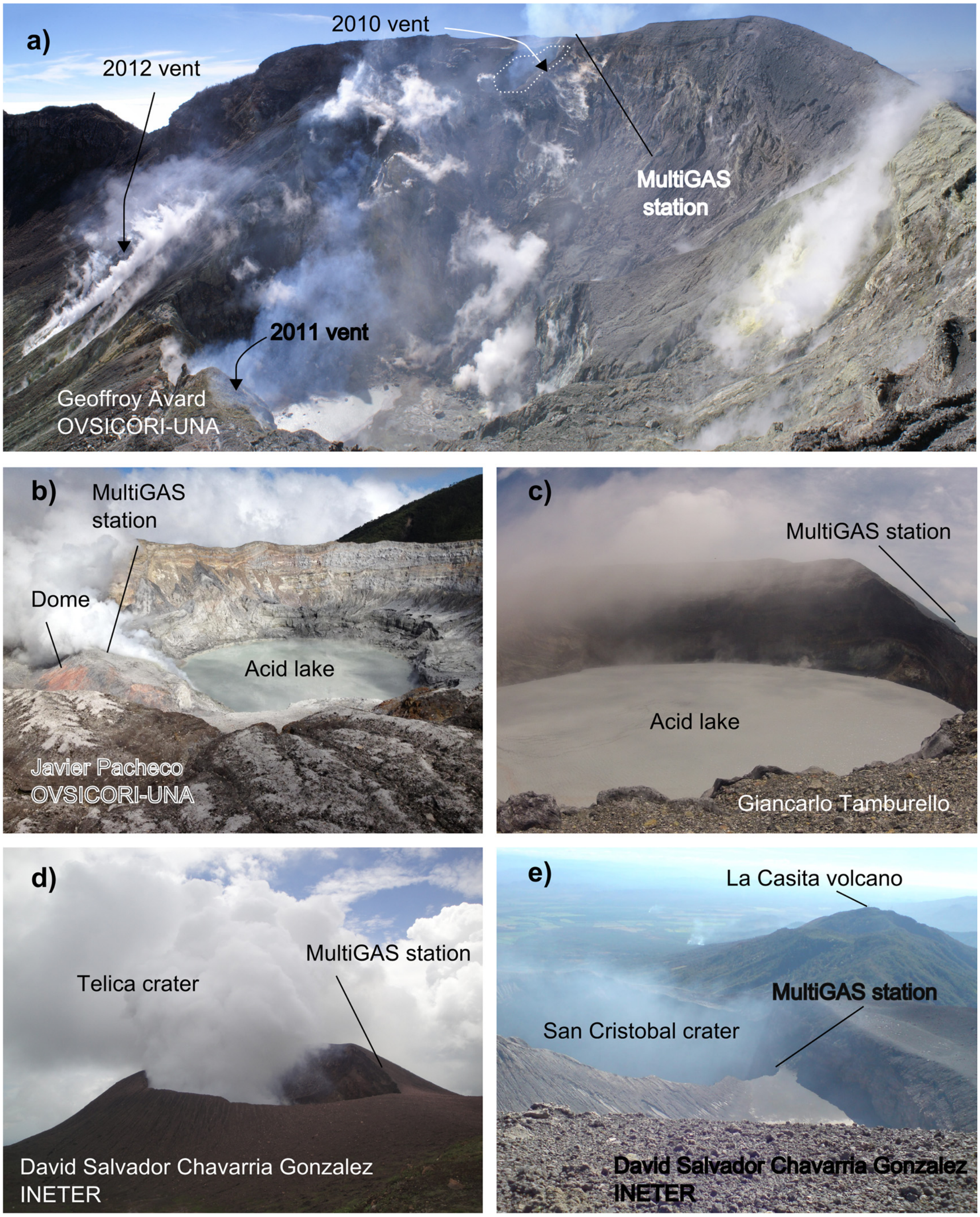

Fig. 2. Degassing activities at the summit craters of the five investigated volcanoes, and the positions of the Multi-GAS instrument: (a) Turrialba, (b) Poás, (c) Rincón de la Vieja, (d) Telica, and (e) San Cristóbal. The credits are shown in the figure.

Table 1

Time-averaged compositions of volcanic gas plumes at the five investigated volcanoes. The quoted ratios (all molar) are arithmetic mean±SD values for the data reported in Fig. 4 (except for Rincón de la Vieja, where only one acquisition was available). Vent temperatures were measured using portable IR cameras, and should be viewed as the minimum temperatures of the vents feeding the plumes (see Fig. 2).

Country	Date	Volcano	Peak vent temperature (°C)	CO_2/SO_2	H_2O/CO_2	SO_2/H_2S
Costa Rica	March 12–19, 2013	Turrialba	590 (vent 2010) to ∼790 (vent 2012)[a]	2.2 ± 0.8	20.4	n.d.
Costa Rica	April 2–4, 2013	Turrialba	∼500 (vent 2010) to ∼800 (vent 2012)[a]	2.0 ± 0.3	32.0	n.d.
Costa Rica	April 8, 2013	Rincón de la Vieja	∼130[a]	27.0 ± 15.3[*]	201	1.10 ± 0.15
Costa Rica	April 16–18, 2013	Poás	∼500[a]	0.30 ± 0.06	175	9.9 ± 2.7
Nicaragua	March 27 to April 4, 2013	Telica	∼507[b]	3.0 ± 0.9	21.7	n.d.
Nicaragua	April 11–16, 2013	San Cristóbal	500[b]	4.2 ± 1.3	22.0	n.d.

Data source: [a] OVSICORI-UNA (2013); [b] INETER (2013).
[*] This converts into a CO_2/S_T ratio of 14.2 ± 9.0, using a SO_2/H_2S ratio of 1.10 ± 0.15.

Table 2
SO_2 fluxes (measured by UV spectroscopy) and calculated CO_2 fluxes (from multiplication of SO_2 fluxes and time-averaged CO_2/SO_2 ratios). The same table also reports literature data from Momotombo and Masaya volcanoes, which we use for inferring total outputs from Costa Rica (CVS), Nicaragua (NVS) and the entire Costa Rica–Nicaragua volcanic arc segment (CNVS). See text for discussion.

Country	Date	Volcano	CO_2/SO_2	SO_2 flux (tons/day)	CO_2 flux (tons/day)
Costa Rica	March 12–19, 2013	Turrialba	[a]	840 ± 120[b]	1270 ± 700
Costa Rica	April 2–4, 2013	Turrialba	[a]	668 ± 308[c]	918 ± 560
Costa Rica	March–April 2013	Turrialba, mean	[a]	754 ± 214[b]	1094 ± 631
Costa Rica	April 16–18, 2013	Poás	[a]	124 ± 30[b]	25.5 ± 11.0
CVS		**Total output**		$\mathbf{878 \pm 244}$	$\mathbf{1120 \pm 642}$
Nicaragua	March 27 to April 4, 2013	Telica	[a]	64 ± 34[c]	132 ± 109
Nicaragua	April 11–16, 2013	San Cristóbal	[a]	181 ± 35[b]	523 ± 263
Nicaragua	1982–1985	Momotombo	2.6[d]	73[e]	130
Nicaragua	1998–2009	Masaya	2.6 ± 0.7[f]	690 ± 182[f]	930 ± 350[f]
NVS		**Total output**		$\mathbf{1008 \pm 251}$	$\mathbf{1715 \pm 722}$
CNVS		**Total output**		$\mathbf{1886 \pm 495}$	$\mathbf{2835 \pm 1364}$

Data source: [a] From Table 1 (this study); [b] This study; [c] This study and Conde et al. (in press); [d] Average of gas compositions reported by Menyailov et al. (1986); [e] From Andres and Kasgnoc (1998); [f] Time-averaged (1998–2009) flux and composition from Martin et al. (2010).

the SO_2 flux dropped to approximately 1000 tons/day, and by April 2013 it had decreased even further, to 181 ± 35 tons/day.

5. Results

The Multi-GAS-derived concentration data were post-processed to calculate the ratios of various volatiles using the procedure described by Aiuppa et al. (2006, 2010). Fig. 3a–e are scatter plots of CO_2 vs. SO_2 mixing ratios for the 5 explored volcanoes. We use raw data for SO_2 and background-corrected mixing ratios for CO_2. The latter were obtained from raw data by subtracting ambient air mixing ratios that were determined in "blank" sites upwind of the vents.

CO_2 vs. SO_2 compositions for the entire measurement intervals (open symbols in Figs. 3a–d) exhibited significant scatter at each volcano, implying substantial CO_2/SO_2 ratio variations over timescales of hours/days. Subsets of data acquired during shorter intervals, of 240–480 s each (examples of which are given by the populations of filled data-points in Figs. 3a–d), showed more restricted compositional ranges, instead. We therefore calculated the slopes of the best-fit regression lines in each of these subintervals (see examples in Fig. 3) to obtain the time-averaged (temporal windows of 240–480 s) CO_2/SO_2 ratios. No ratio was calculated during sub-intervals when there was excessive dilution of volcanic gases by atmospheric gases (e.g., for SO_2 mixing ratios <4 ppmv in (a) to (d)), or when a low correlation coefficient ($R^2 < 0.7$) was obtained. The procedure was optimized and automated by using the Ratiocalc software (https://sites.google.com/site/giancarlotamburello/volcanology/ratiocalc), which allowed to scan the entire data set and create sequences of scatter plots for distinct subintervals.

The so-obtained time series of CO_2/SO_2 ratios are shown in Fig. 4 for the volcanoes where the fixed Multi-GAS was deployed. At Turrialba (Fig. 4a) we obtained plume CO_2/SO_2 ratios ranging from 0.7 to 4.4 (all ratios quoted here and below are on a molar basis). Following Conde et al. (in press), we attribute this range of bulk plume compositions to the involvement of multiple, compositionally distinct gas sources. Using open-path FTIR, Conde et al. (in press) demonstrated that the level of CO_2 was lower at Vent 2012 ($CO_2/SO_2 \sim 1$) than at Vent 2010 ($CO_2/SO_2 \sim 3$). The majority of the 'bulk plume' Multi-GAS data are comprised between these end-member CO_2/SO_2 ratios. By taking an arithmetic mean of the data set of Fig. 4a, we infer that the overall CO_2/SO_2 ratio for Turrialba was 2.2 ± 0.8 (mean±SD) during March 2013. A slightly lower ratio was observed in early April (2.0 ± 0.3) (Table 1).

The CO_2/SO_2 ratios observed at Telica (3.0 ± 0.9; Fig. 4b) and San Cristóbal (4.2 ± 1.3; Fig. 4c) spread toward CO_2-richer compositions relative to those observed at Turrialba (Table 1). In contrast, a stable, C-poor composition (with a CO_2/SO_2 ratio of 0.30 ± 0.06) was captured by the Multi-GAS at Poás (Figs. 3d and 4d). Finally, the most-extreme CO_2/SO_2 ratios (27.0) in our data set were obtained at Rincón de la Vieja (Table 1 and Fig. 3e), where a very dilute plume ($SO_2 < 2$ ppm) was only detected (leading to smaller correlation – $R^2 = 0.6$ – and larger errors: ±15).

The plume SO_2/H_2S and H_2O/CO_2 ratios (Table 1) were determined using a similar procedure. H_2S was only detected at Poás and Rincón de la Vieja, which allowed for the SO_2/H_2S ratios to be quantified as 9.9 ± 2.7 and 1.10 ± 0.15, respectively. The derived CO_2/S_T ratio ($S_T = SO_2 + H_2S$) at Rincón de la Vieja was therefore 14.2 ± 9.0. Our inferred H_2O/CO_2 ratios for the plume varied over a restricted range (20.4–22.0) at Turrialba, Telica, and San Cristóbal (Table 1). In contrast, more-hydrous compositions (with H_2O/CO_2 ratios of 175–201) were obtained at Poás and Rincón de la Vieja, suggesting possible steam contribution from the active crater lakes.

The SO_2 flux from Turrialba, measured using scanning DOAS spectrometers of the local NOVAC network, was 840 ± 120 tons/day (mean ± SD) during March 12–19 (Table 2), in line with results of previous studies (Campion et al., 2012; Conde et al., 2013, in press). Our inferred SO_2 output from Poás (124 ± 30 tons/day) in 2013 was a factor ~15 larger than measured in 2001 (Zimmer et al., 2004), matching the increasingly active behavior of the volcano since early 2013. The SO_2 outputs from Telica and San Cristóbal averaged at 64 ± 34 and 181 ± 35 tons/day (Table 2).

6. Discussion

6.1. Identification of magmatic fingerprint for the CNVS

The compositional features of magmatic gases in the CNVS have been studied from direct sampling of fumaroles (Menyailov et al., 1986; Rowe et al., 1992; Zimmer et al., 2004; Elkins et al., 2006; Fischer et al., 2007) or via Fourier-transform infrared (IR; FTIR) spectroscopy (e.g., Masaya Volcano; Burton et al., 2000; Martin et al., 2010). The CO_2/S_T composition of these CNVS gases is reported in Fig. 5a, which includes both hot- and low-temperature crater fumaroles.

Low-temperature (<100 °C) fumarolic gases are a source of key information on inert (Zimmer et al., 2004; Elkins et al., 2006) and/or poorly reactive (e.g., CO_2) (Shaw et al., 2003) gases, but their deep CO_2/S_T magmatic fingerprint may in some cases be obscured by selective scrubbing of water-soluble S (Symonds et al., 2001): this is reflected by the high CO_2/S_T ratios (≫1000) in some of the low-T crater gas manifestations (Fig. 5a). The Turrialba summit fumaroles of Vaselli et al. (2010) for example, being thought by those authors to sit at the hydrothermal–magmatic transition (temperatures of 86–282 °C), still show a large range of CO_2/S_T ratios (1.5–3803), particularly for the low-temperature samples (Fig. 5a). The same interactions of magmatic gases with lake and groundwater systems probably also explain the CO_2-rich signature of our Rincón de la Vieja gas (Table 1).

Our reported compositions (Table 1) show a restricted range of (relatively low) CO_2/S_T ratios (0.3–4.2; Fig. 5a). Also, given the relatively high emission temperatures of the gas manifestations, we consider that our gas composition was only marginally affected by secondary scrubbing processes. One possible exception is San Cristóbal, where a temperature of only 105 °C was reported during April 2013 (INETER, 2013); however, these observations were limited by poor visibility inside the crater. The persistence of perceptible sound irradiating from the crater (INETER, 2013), the lack of H_2S in the plume, and the reported temperatures being >500 °C only a few months previously support high-temperature, open-vent degassing activity during April 2013, and a minor effect of gas scrubbing processes.

Fig. 5 is also suggestive for that high-temperature gas samples from Costa Rica and Nicaragua (both our data and those of previous studies) plot along two distinct compositional domains. In Fig. 5b, which includes the subset of ≥185 °C gases, the temperature dependences of CO_2/S_T ratios from Nicaraguan and Costa Rican volcanic gas are shown by equations, along with their relative lower and upper 50% prediction bounds. The best-fit regression lines and their confidence intervals give rise to two distinct (and nearly parallel) compositional arrays. This suggests that, apart from some very minor overlap (see dashed area in Fig. 5b), the distinction between the two data clusters is statistically significant at 50% confidence level. The two data clusters remain distinct also if a higher cut off temperature (500 °C) is used to focus on 'truly magmatic' gases (Fig. 5c), which typically exhibit no temperature dependence. These trends converge at high temperatures to CO_2/S_T ratios of ∼3 and 0.5–1.0 for Nicaragua and Costa Rica, respectively, and are therefore suggestive of a distinct, CO_2-richer magmatic gas signature in Nicaragua relative to Costa Rica (Fig. 6a).

We caution that, given the paucity of data available and the (minor) data overlap in Fig. 5, we cannot entirely rule out coalescence of the fields as more data becomes available. To obtain more high-temperature gas information, especially in Costa Rica, clearly remains to be prioritized by future gas studies. We still observe that diffuse soil CO_2 degassing, which contributes to only 8% (Poás) to 16% (Turrialba) of crater plume emissions (De Moor J.M., pers. data), cannot compensate against the more C-poor gas signature in Costa Rica (relative to Nicaragua). We additionally argue that the melt inclusion (MI) record of the contents of volatiles in CNVS magmas (Fig. 6b, c) is well consistent with the volcanic gas information.

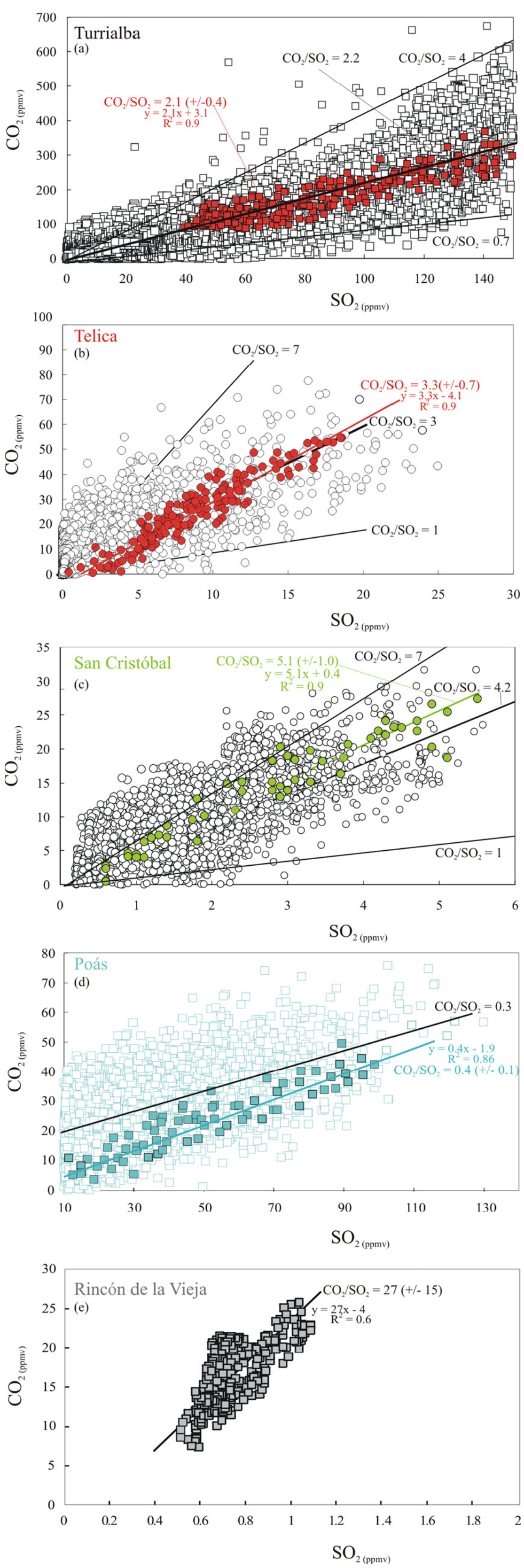

Fig. 3. Scatter plots of CO_2 versus SO_2 mixing ratios (in ppmv) for the five volcanoes investigated. CO_2 mixing ratios are after subtraction of background-air mixing ratios. In panels (a) to (d), we show with "open symbols" the complete data set of simultaneous CO_2–SO_2 detections collected during the entire Multi-GAS exposure period (we do not show results for measurement intervals with no plume). In each plot, the filled symbols demonstrate an example of the procedure used to calculate the CO_2/SO_2 (molar) ratio (shown in Fig. 4): a specific sub-subset of data (temporal window of 240–480 s) is selected, and the corresponding averaged CO_2/SO_2 ratio in that temporal interval is calculated from the slope of the best-fit regression line (color lines in panels (a) to (d); the same panels show equation of the regression lines, the correlation coefficients (R^2) and the errors of the CO_2/SO_2 ratio for the displayed sub-sets of data). The procedure was extended to the entire data set (using the software ratiocalc), but ratios are only displayed (in Fig. 4) for specific temporal intervals with high regression coefficients ($R^2 > 0.7$). The plots also show, for each volcano, the mean CO_2/SO_2 ratio (thick black line; arithmetic mean of the ratios displayed in Fig. 4a–d) and the minimum–maximum ratios obtained (thin solid lines; minimum and maximum ratios in Fig. 4a–d). For Rincón de la Vieja, the grey symbols refer to the entire data set acquired (regression line – color line – correlation coefficients (R^2) and errors of the CO_2/SO_2 ratio are also displayed).

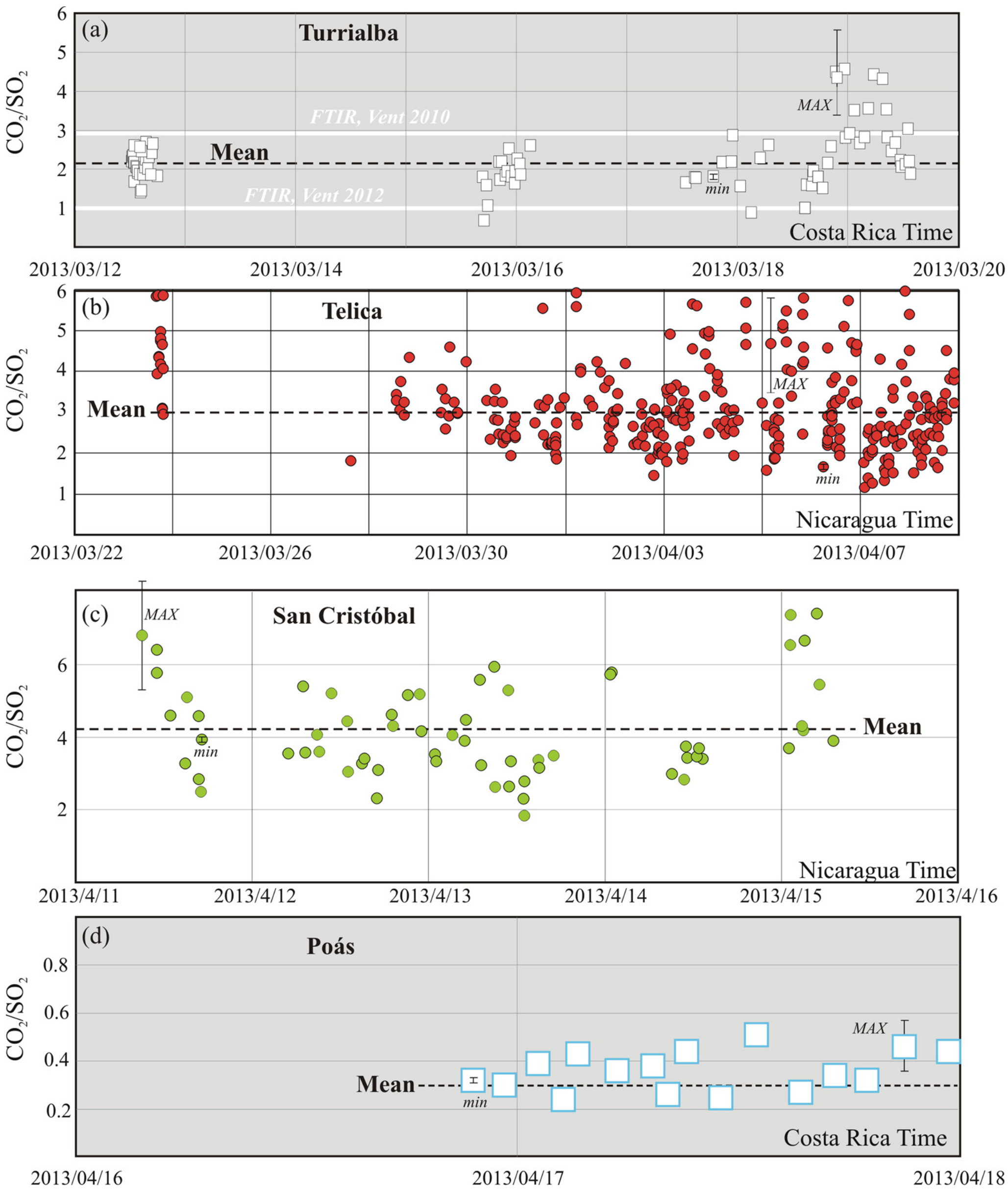

Fig. 4. Time series of the (molar) CO_2/SO_2 ratios recorded at the four volcanoes where the fully autonomous Multi-GAS was temporarily deployed. In each panel, each single data-point represents the time-averaged ratio obtained from sub-sets of data acquired within sub-intervals of 240–480 s (see examples of procedure for calculating the ratios illustrated in Fig. 3). The errors associated to each ratio are always lower $\leq$15% (minimum and maximum relative errors for each volcano data set are shown in the figure as error bars, labeled min and max, respectively). For Turrialba (panel a), we also show the inferred compositions for Vent 2012 ($CO_2/SO_2 \sim 1.1$) and Vent 2010 ($CO_2/SO_2 \sim 2.9$), as obtained by active open-path FTIR and reported in Conde et al. (in press). Most Multi-GAS data fall between these two extremes, indicating their spread of ratios reflect variable mixing between 2010 and 2012 gases. Higher (>3) ratios, particularly after March 19, probably reflect transient, sporadic gas contributions from other low-temperature gas sources such as fumaroles and steaming grounds. The time-averaged (mean) ratios, shown for each volcano and also reported in Table 1, are simple arithmetic mean values of the data reported in each panel.

Extracting from MIs information on CO_2 contents in source (mantle) magmas is complicated by a number of processes, including pre- and post-entrapment crystallization (Kelley et al., 2006, 2010), post-entrapment CO_2 sequestration into bubbles, and pre-eruptive CO_2 degassing (see Hartley et al., 2014 for an updated list of references). Of these, pre-eruptive degassing is more difficult to account for, so that measured CO_2 contents in MIs typically underestimate CO_2 contents in primitive (un-degassed) mantle melts. With these precautions in mind, we still observe that CO_2/S_T (molar) ratios in MIs from the CNVS (data from Wade et al., 2006; Benjamin et al., 2007 and Wehrmann et al., 2011) exhibit along-arc variations in all parallel to those shown by volcanic gases (Fig. 6b). The estimated parental magma CO_2 compositions (which we calculated from MIs using the procedure of Portnyagin et al., 2007 and Watt et al., 2013) also are consistent with such distinct CO_2-signatures (Fig. 6c).

In summary, although quantification of pre-eruptive CO_2 degassing remains an issue (for MIs) and more data are highly needed (for both gases and MIs) to corroborate our conclusions, we conclude that both volcanic gases and MIs concur to suggest that the CO_2/S_T-ratio signature for magmatic volatiles is higher for Nicaragua than for Costa Rica. It should be noted from Fig. 1 that the transition from CO_2-poor (Costa Rica) to CO_2-rich (Nicaragua) gases broadly corresponds to the Fisher Ridge, which is a structural discontinuity interpreted by Husen et al. (2003) as marking a compositional transition zone (distinct hydration states) in the mantle wedge. We return to the potential factors determining this compositional variability in Section 6.3.

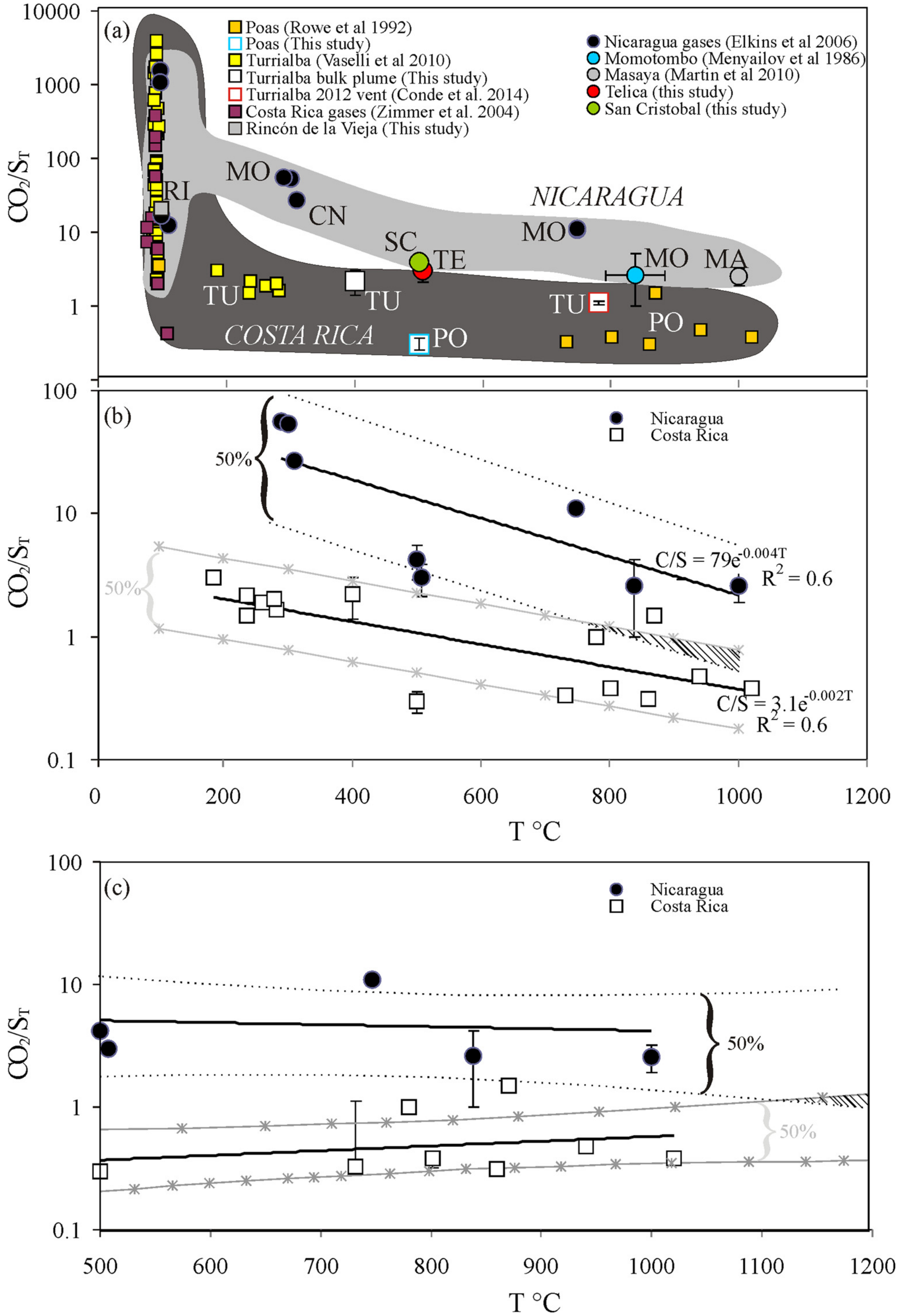

Fig. 5. (a) CO_2/S_T molar ratios of volcanic gases (from the literature) and plumes (this work) for Nicaragua (squares) and Costa Rica (circles), plotted versus the corresponding discharge temperatures. Where possible, a vertical error bar is displayed (one standard deviation of the mean value). S_T was calculated as the sum of measured SO_2 and H_2S (both for plumes and fumarolic gases). From the data sets of Zimmer et al. (2004) and Elkins et al. (2006), we only extracted their crater fumarole (FC type) samples and their (high-T) Momotombo power-plant samples. For the volcanic gas plumes, we used estimated temperatures of the source vents obtained using portable IR cameras. In the specific case of Turrialba, we show two independent compositions: (a) the composition of Vent 2012 measured by Conde et al. (in press) using FTIR ($CO_2/S_T = 1.1$; temperature = 790 °C) and (b) our own time-averaged bulk plume composition ($CO_2/S_T = 2.2$; Table 1), for which we assumed a source minimum temperature of 400 °C (the temperature of Vent 2010, which was clearly the source of most of the gas emitted). For San Cristóbal, we tentatively used the vent temperature (500 °C) measured in December 2012 (visibility was very low inside the crater during our April survey, which only allowed a minimum temperature of 105 °C to be determined). The diagram demonstrates a large spread of ratios in low-temperature gas manifestations, indicating the presence of secondary processes. High-temperature gases have a narrower range of CO_2/S_T ratios, and depict two distinct evolution trends for Nicaragua and Costa Rica; (b) a zoom of (a) for the selection of high-temperature (≥185 °C) gases. Nicaraguan and Costa Rican gases exhibit exponential decreases in CO_2/S_T ratios with increasing temperatures (see regression equations and R^2) that converge to distinct values of ≥3 (Nicaragua) and ≤1 (Costa Rica). The lower and upper 50% prediction bounds of the regression curves are also shown (see curves labeled "50%"). These intervals indicate that there is 50% chance that any new observation is actually contained within the lower and upper prediction bounds. The dashed area marks a small region of overall between the two distributions; (c) same as (b) but using a cut off temperature of 500 °C to specifically focus on magmatic gases.

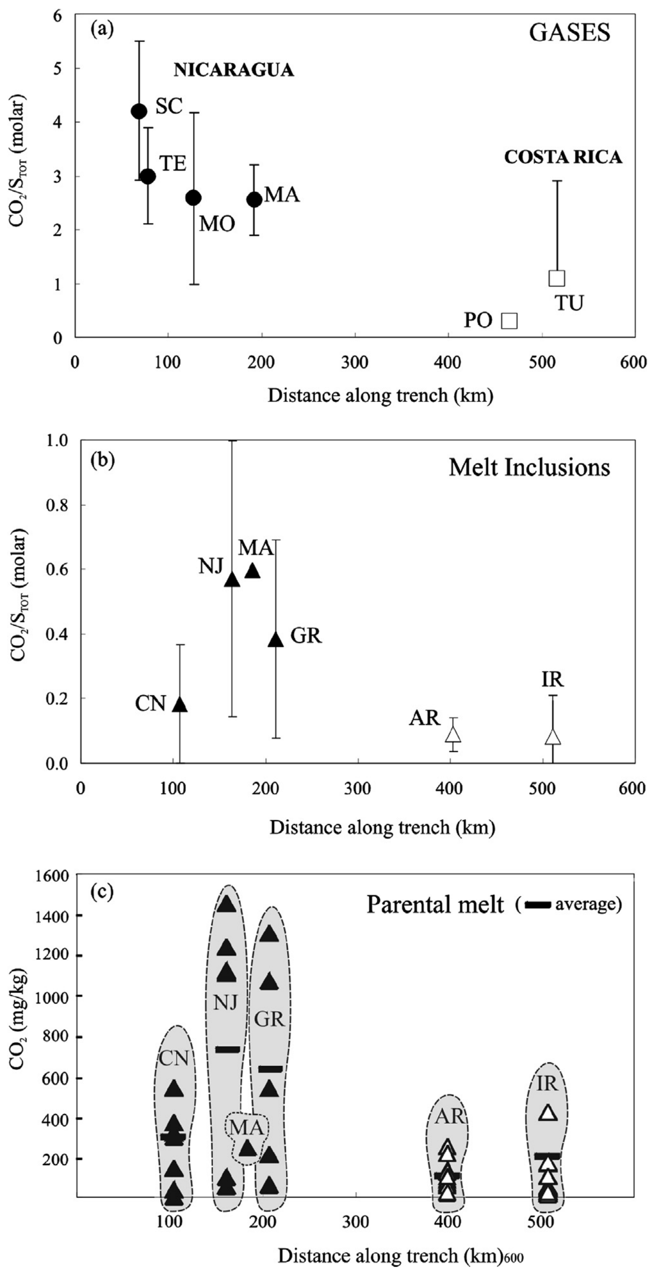

Fig. 6. (a) Along-arc variations of volcanic gas CO_2/S_T (molar) ratios. Distances along the arc are from north to south from the Cosigüina volcano in Nicaragua. This figures includes data for high-temperature (≥400 °C) gases only. Data for Poás (PO), Telica (TE) and San Cristóbal (SC) are mean ± SD from this study (Table 1). For Momotombo (MO) and Masaya (MA), we report averaged (mean±SD) compositions from Menyailov et al. (1986) and Martin et al. (2010), respectively. For Turrialba (TU), we show the mean gas composition for the 2012 vent (Conde et al., in press), which (given its high-temperature – 790 °C) is more representative of the magmatic gas signature. The vertical bar also includes the range of CO_2/S_T ratios measured in this study (2.2 ± 0.8). (b) Along-arc variations of CO_2/S_T (molar) ratios in MIs are displayed for comparison. Data on MIs (corrected for post-entrapment crystallization) are from Wade et al. (2006), Benjamin et al. (2007) and Wehrmann et al. (2011) (we omitted three evolved – $SiO_2 > 57\%$ – MIs from Irazù of Wehrmann et al., 2011, having unusually low S contents). Other volcanoes displayed are: CN = Cerro Negro; NJ, Nejapa; GR = Granada; AR = Arenal; IR = Irazú. (c) Along-arc variations in CO_2 contents in parental magmas from the CNVS. These were estimated correcting MI contents for pre-entrapment crystallization using the procedure of Portnyagin et al. (2007) and Watt et al. (2013). This involved adding olivine to the melt inclusion compositions until equilibrium with mantle olivine (Fo_{90}), using PETROLOG and the Ford et al. (1983) olivine model (fO_2 values from source MI data sets). The so-estimated parental magma CO_2 contents of figure (c) are likely under-estimates of the real CO_2 contents in source (mantle) magmas, since pre-entrapment CO_2 degassing is not accounted for. Still, the diagrams of (a) to (c) support a CO_2-richer composition of volcanism in Nicaragua relative to Costa Rica.

6.2. CO_2 output

The volcanic CO_2 output for each of our monitored volcanoes except Rincón de la Vieja was obtained by scaling the mean CO_2/SO_2 ratio to the co-acquired SO_2 flux data (Table 2). Our inferred CO_2 fluxes ranged from low (Poás: 25.5 ± 11.0 tons/day) to moderate (Turrialba: 918 to 1270 tons/day) (see Burton et al., 2013 for the typical CO_2 outputs from individual volcanoes). Our estimated CO_2 flux for Poás compares well with the CO_2 flux (33.6 tons/day) quoted by Zimmer et al. (2004) for March 2001, a time during which low SO_2 emissions (8.3 tons/day) were compensated by high CO_2/SO_2 ratios (5.9), presumably as a result of increased hydrothermal scrubbing of SO_2 during 2001 when fumaroles temperatures were also lower. Based on these values, Turrialba ranks as the largest volcanic CO_2 emitter in the CNVS, even exceeding the time-averaged contribution from Masaya (Martin et al., 2010). The CO_2 output for San Cristóbal is, for comparison, a factor ∼2 lower (523 ± 263 tons/day; Table 2).

6.2.1. Implications for the present-day CO_2 output from the CNVS

Our measurements reported here add new information to the currently incomplete volcanic CO_2 flux data set (Burton et al., 2013), and can serve as a basis for refining previous assessments of the volcanic CO_2 output from the CNVS. Hilton et al. (2002) reported on procedures for calculating the CO_2 output from individual arc segments based on extrapolation of available SO_2 flux data sets (Andres and Kasgnoc, 1998), and on the assumption that the distribution of SO_2 emissions follows the power law (Brantley and Koepenick, 1995). For the CAVA, they estimated a CO_2 output of ∼3600 tons/day. One possible source of uncertainty in the methodology of Hilton et al. (2002) is that a representative CO_2/SO_2 ratio for each arc segment has to be assumed in order to convert the SO_2 output into the CO_2 output. However, precise knowledge of these arc-averaged gas ratios is limited by the incomplete volcanic gas data set that is available, and by inadequate information on temporal and geographic (Fig. 6a) variability in the gas composition. Hilton et al. (2002) used a representative CO_2/S_T ratio of 2.7 for the CAVA, which, while close to our inferred magmatic signature for Nicaragua, appears unrepresentative (i.e., too rich in C) of Costa Rica gas (Fig. 6a). A lower CO_2/S_T ratio of 1.0–2.2 was proposed for the CAVA by Mather et al. (2006).

In light of the above-mentioned considerations, here we assess the total CO_2 output from the CNVS as a simple sum of the calculated CO_2 fluxes from individual volcanoes (Table 2). For Costa Rica, we infer a combined flux from Turrialba plus Poás of 1120 ± 642 tons/day (the average during March and April was used for Turrialba; Table 2). This value does not take into account emissions from Costa Rican volcanoes for which measurements are not available, or diffuse degassing from the flanks of volcanoes, and is therefore conservative in that it underestimates the total CO_2 output from CVS. The SO_2 flux was unfortunately not determined at Rincón de la Vieja, for example, so that the CO_2 contribution from this volcano remains undetermined. However, we consider that – at least in the conditions observed during March 2013 – Turrialba and Poás were the dominant sources of volcanic CO_2 in Costa Rica. Arenal Volcano, which has been degassing for years (Williams-Jones et al., 2001), was emitting <1 tons/day SO_2 during spring 2013 (OVSICORI-UNA, 2013). No visible plume was seen at any other volcano (e.g., Barva, Tenorio, Planatar) including Irazù, where only weak hydrothermal fuming persists (OVSICORI-UNA, 2013). We additionally note that our inferred total CO_2 output from CVS in 2013 is still larger than that (354–774 tons/day) measured by Zimmer et al. (2004) in 2001, when the (extrapolated) SO_2 flux was of only 191 tons/day (they used CO_2/S_T-ratio proxies for CVS of respectively 2.7 and 5.9) (Table 3).

Table 3
Summary of volcanic CO_2 output estimates for the NVS, CVS, and CNVS.

NVS CO_2 output (tons/day)	CVS CO_2 output (tons/day)	CNVS CO_2 output (tons/day)	Source	Procedure
Present-day fluxes				
–	–	3618	Hilton et al. (2002)	Gas composition (CO_2/S_T-ratio proxy of 2.7) + extrapolated SO_2 flux (3740 tons/day) for CAVA. The CAVA total CO_2 flux of 6932 tons/day of Hilton et al. (2002) was scaled to the total length of the CNVS (540 km) to obtain the CO_2 output for this arc segment.
–	354–774	–	Zimmer et al. (2004)	Gas composition (CO_2/S_T-ratio proxies for CVS of respectively 2.7 and 5.9) + extrapolated SO_2 flux (191 tons/day)
2411	–	–	Elkins et al. (2006)	From ^{3}He flux and arc length
14 500	–	–	Elkins et al. (2006)	Gas composition (CO_2/S_T ratio of 13) + extrapolated SO_2 flux (1700 tons/day)
		2296–5010	Mather et al. (2006)	Gas composition (CO_2/S_T ratio of 1.0–2.2) + extrapolated CAVA SO_2 flux (4360 tons/day). Note that the total CAVA flux of 4400–9600 tons/day reported by Mather et al. (2006) was scaled to the total length of the CNVS (540 km)
1715 ± 722	**1120 ± 642**	**2835 ± 1364**	**This study**	Sum of measured fluxes from individual volcanoes (from Table 2)
Geological fluxes				
–	–	1231	Wehrmann et al. (2011)	MI composition and magma eruption rate
319	26	345	Freundt et al. (in press)	MI composition and magma eruption+intrusion rate
3004	**180**	**3184**	**This study**	Combining the petrologically estimated S output of Freundt et al. (in press) (1457 tons/day and 261 tons/day for NVS and CVS, respectively) with our inferred magmatic gas compositional proxies of Nicaragua (CO_2/SO_2 = 3) and Costa Rica (CO_2/SO_2 = 1)

To calculate the CO_2 output for the NVS, we combined our Telica and San Cristóbal results with the recently reported CO_2 output from Masaya of 930 ± 350 tons/day (Martin et al., 2010). In our calculation we included a potential CO_2 contribution from Momotombo of 130 tons/day CO_2, calculated using the SO_2 flux of 73 tons/day reported by Andres and Kasgnoc (1998), and a CO_2/SO_2 molar ratio of 2.6 (the mean value of the Menyailov et al., 1986 data set; for comparison, a CO_2 flux of 120 tons/day was estimated for 1982 by these authors). Again we neglected the contributions from other volcanoes, since no visible plume or substantial gas manifestations were observed (INETER, 2013). Our calculated CO_2 output for the NVS of 1715 ± 722 tons/day is nearly one order of magnitude lower than that estimated by Elkins et al. (2006) (14 500 tons/day; Table 3), who adopted an high CO_2/SO_2 ratio of 13 in their calculations. According to our new data and calculations, the total CO_2 output from the CNVS during March and April 2013 was 2835 ± 1364 tons/day (Table 2), which is of the same range as the estimate of ∼3600 tons/day reported by Hilton et al. (2002) (Table 3).

6.2.2. CO_2 output from the CNVS over geological timescales

One obvious limitation of gas-based CO_2 output calculations is the relatively short observation period (days, in our specific case) on which they are based. To what extent campaign data – such as those presented here – can be extrapolated to long-term volcano degassing behavior remains questionable. For example, our finding of the CO_2 output for CVS being larger in 2013 than that measured in 2001 by Zimmer et al. (2004) clearly results from the present degassing unrest at Turrialba Volcano, which however only started in 2008 following more than a century of weak fumarolic activity (Vaselli et al., 2010; Campion et al., 2012; Conde et al., 2013). Therefore, the temporal stability of our estimate of ∼1200 tons/day for the CO_2 output from CVS remains uncertain.

Investigations of volatiles based on MI studies and long-term magma eruption rates (e.g., Wallace, 2005) cover time intervals ranging from years to tens of thousands of years, and are therefore in principle more suitable for inferring the long-term budgets of volatiles at arc segments. However, MI-based CO_2 output estimates are likely to be affected by pre-entrapment degassing, which can be very large for poorly soluble volatiles such as CO_2 (Papale, 2005). For example, Wehrmann et al. (2011) presented CO_2 compositional data for a suite of MIs from the CAVA, and calculated an arc-length-normalized CO_2 output of 2.6×10^{-2} g/m/s. In the very approximate assumption of a constant magma production rate (intrusive + extrusive) along CAVA, and for a ∼600-km-long CNVS, this would correspond to an average CO_2 output of 1230 tons/day, or a factor ≥3 lower than gas-based estimates (Table 3). An even lower CO_2 output (345 tons/day) can be inferred from the recent compilation of Freundt et al. (in press), who refined the earlier CO_2 output inventories by considering magma intruded in the crust in addition to magma erupted, and used specific CO_2/K_2O in MIs for the different arc segments (Wehrmann et al., 2011 used instead the Nicaraguan maximum CO_2/K_2O values for the entire volcanic front). Overall these results suggest that variable extents of pre-entrapment CO_2 degassing in MIs (Wehrmann et al., 2011) only allow for minimum estimates of the total CO_2 output to be inferred on the basis of petrology. Large pre-eruptive CO_2 degassing at depth, at conditions where S is mostly retained in the silicate melt, is also consistent with the CO_2/S_T ratios being far lower in CNVS MIs (Fig. 6b) than in the corresponding gases (Fig. 6a).

One possible method to resolve the conundrum of pre-entrapment CO_2 degassing is to combine petrologically estimated SO_2 outputs with our inferred magmatic gas CO_2/S_T proxies (Figs. 5 and 6a). Freundt et al. (in press) found that the long-term SO_2 output from the CNVS calculated on the basis of petrology – from the MI composition and the magma production rate – is 1718 tons/day (1457 tons/day and 261 tons/day for NVS and CVS, respectively; Table 3). We converted these SO_2 output fluxes into CO_2 output fluxes using our best estimates for the magmatic gas CO_2/S_T-ratio signature in Nicaragua and Costa Rica; values of 3 and 1, respectively, yielded a long-term CO_2 output of ∼3184 tons/day for the CNVS, with a dominant contribution from CO_2-rich volcanism in Nicaragua (∼3000 tons/day). We conclude that present-day (gas-based) and geological (petrology-based) CNVS CO_2 outputs are in very close agreement in our case (2835 ± 1364 vs. 3184 tons/day; Table 3). We additionally infer from Table 3 that, while total CNVS emissions are fairly similar in the two estimates, the present-day (gas) emissions in Costa Rica (Nicaragua) are somewhat more (less) intense than the long-term (petrologic) time-averages.

6.3. Factors controlling along-arc variations in gas chemistry

It has been shown that there are large and systematic along-arc variations in several parameters at the CAVA, including the age and geometrical properties of the slab (Protti et al., 1994; Syracuse and Abers, 2006), the extent of serpentinization of the subducted mantle (Rüpke et al., 2004; Freundt et al., in press), and the crust thickness (MacKenzie et al., 2008). In response to such changing subduction conditions, the magma compositions also vary substantially along the arc (Plank and Langmuir, 1988; Carr et al., 1990, 2003; Patino et al., 2000; Rüpke et al., 2002; Eiler et al., 2005). Research (Sadofsky et al., 2008) has identified that multiple distinct slab (essentially sediments, altered oceanic crust, and serpentinized mantle) and mantle wedge components are involved in magma generation. However, the general consensus is that slab-derived fluids play the most-significant role in the generation of Nicaragua magmas (Plank and Langmuir, 1998; Plank et al., 2002), whereas a more MORB-type magmatism occurs in Costa Rica, possibly also due to underplating of the uppermost part of the sediment column beneath the overriding crust (Leeman et al., 1994). For example, high $^{10}Be/^{9}Be$, U/Th, and Ba/La ratios in lavas all point to a larger volume of trench sediments being subducted in Nicaragua, where the accretionary prism is also more significant (von Huene et al., 2000). These variable fluid contributions from the slab are also thought to control the along-arc variations in the signature of volatiles of CAVA magmas (Sadofsky et al., 2008; Wehrmann et al., 2011; Freundt et al., in press) and gases (Fischer et al., 2002, 2007; Shaw et al., 2003; Zimmer et al., 2004; Elkins et al., 2006), which all exhibit more sedimentary affinity in Nicaragua.

The present study is the first to attempt to extend the characterization of along-arc variations at the CAVA to major elements (CO_2 and S) in high-temperature magmatic fluids. The obtained results – although requiring additional measurements and studies – are suggestive of the existence of a distinct CO_2/S_T-ratio signature in magmatic gases of the CNVS (Fig. 6a), and likely imply involvement of different sources of volatiles in the two arc segments. Isotopic studies of CAVA cold-gas manifestations (Fischer et al., 2002, 2007; Shaw et al., 2003; Zimmer et al., 2004; Elkins et al., 2006) have revealed a more slab-like isotopic signature of the emitted N_2 and CO_2 in Nicaragua relative to the more-MORB-like signature of Costa Rica gas. In particular, Zimmer et al. (2004) and Elkins et al. (2006) used mass and isotopic balance considerations to calculate the fraction of slab-derived N_2 released from each of the major volcanic and geothermal systems in the CNVS. Fig. 7a indicates that our magmatic gas CO_2/S_T ratios are positively correlated with the calculated N_2 sedimentary fractions of Zimmer et al. (2004) and Elkins et al. (2006). Similarly, Shaw et al. (2003) and Hilton et al. (2010) used He–C systematics to calculate the relative contributions of slab-derived C (from both limestone and organic sediments) and mantle-derived C to the chemistry of Central American gas samples. Their calculated fractions of limestone-derived C, shown in Fig. 7b, are also consistent with our inferred magmatic gas CO_2/S_T ratios. We finally argue from these correlations that the transition from a CO_2-poor (Poás) to a CO_2-rich (San Cristóbal and Telica) volcanic gas composition is well explained by increasing additions of CO_2-rich slab fluids to the mantle wedge.

To explore this possibility further, we analyzed the discrepancy in the volcanic gas CO_2/S_T ratio between Nicaragua and Costa Rica in relation to the composition of the inputs of volatiles at the Central American subducting slab. An extensive compilation of these input flux data has recently been presented by

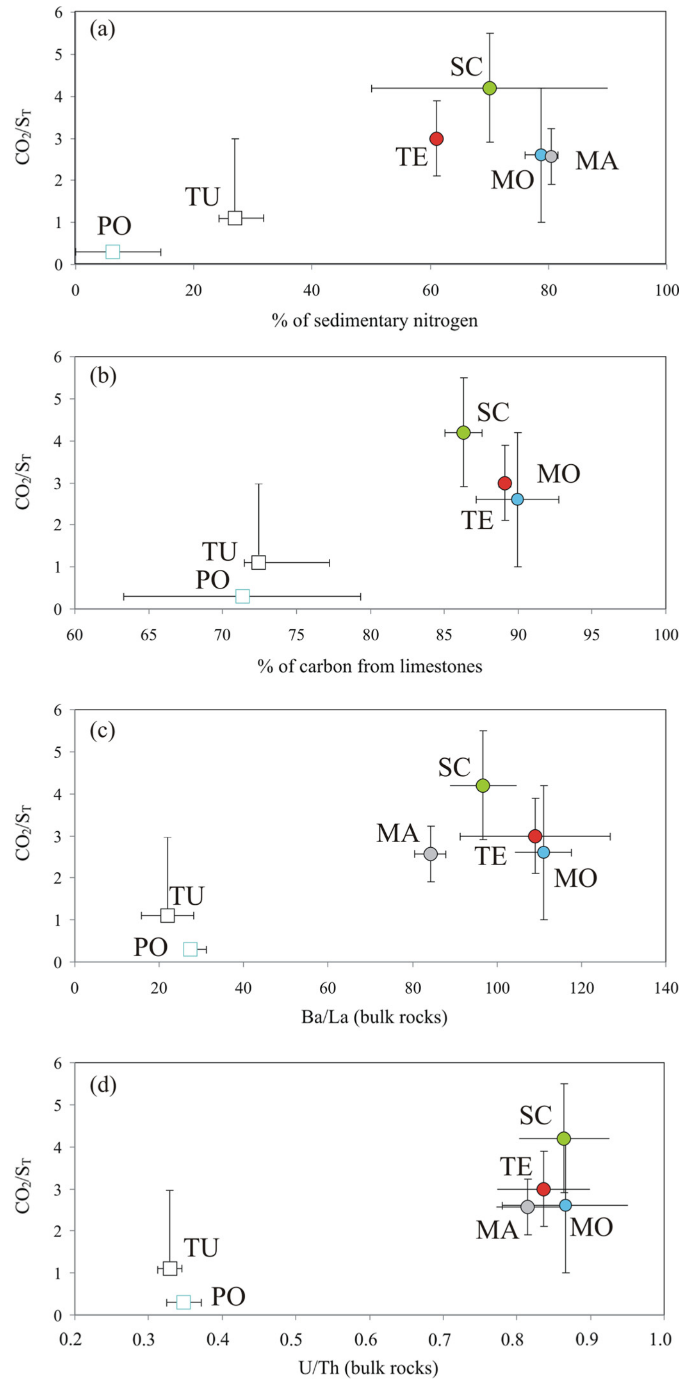

Fig. 7. Scatter plots displaying correlations between the magmatic gas CO_2/S_T-ratio signature of each volcano (same high-temperature gas data as in Fig. 6) and geochemical/petrologic tracers of slab-derived fluids. For each parameter, the mean ± 1 SD are shown. The considered proxies of slab fluid addition are (a) the percentage of sedimentary N_2, corresponding to the fraction of N_2 derived from the slab, calculated from $\delta^{15}N_{N_2}$ and the N_2/He ratios of volcanic gases (the values reported by Zimmer et al., 2004 and Elkins et al., 2006 were averaged for each volcano); (b) the percentage of C from limestone, corresponding to the fraction of C derived from subducted limestone, calculated from $\delta^{13}C_{CO_2}$ and the $C/^{3}He$ ratios of volcanic gases (the data reported by Shaw et al., 2003 and Hilton et al., 2010 for each volcano were averaged); and (c) Ba/La and (d) U/Th ratios in volcanic rocks (we averaged the whole-rock compositions listed in Carr, 1984; Reagan and Gill, 1989; Reagan et al., 1994; Carr et al., 1990; Leeman et al., 1994; Noll et al., 1996; Patino et al., 2000; Hoernle et al., 2008, and Bolge et al., 2009 for each volcano). See Fig. 5 and the caption of Fig. 6 for symbols.

Freundt et al. (in press), who found that the slab-derived fluids had similar CO_2/S_T ratios in Nicaragua (4.4) and Costa Rica (4.0); such a small difference is unlikely to explain the observed along-arc variations in volcanic gas CO_2/S_{TOT} ratios. It is also noteworthy that the estimated CO_2 and SO_2 subduction input fluxes are larger in Costa Rica than in Nicaragua, which is due to higher rates of subduction erosion and faster convergence in the former arc segment (Freundt et al., in press). It is clear that this should lead to a result opposite to the south-to-north increase in CO_2 seen in both MIs and gases (Fig. 6). However, Freundt et al. (in press) also identified sizeable H_2O differences in slab fluids between the two arc segments. In particular, they revealed that the slab fluid was more hydrated in Nicaragua (H_2O = 84 wt%) than in Costa Rica (H_2O = 73 wt%), reflecting a larger extent of mantle serpentinization in Nicaragua (Abers et al., 2003; Grevemeyer et al., 2007). This reflects in the H_2O slab input fluxes being ∼1.6-fold higher in Nicaragua (∼62 Tg/Ma/m) than in Costa Rica (∼39.5 Tg/Ma/m) (Freundt et al., in press).

Following Kerrick and Connolly (2001) and Schmidt and Poli (2003), we therefore assume that a pervasive upward flow of aqueous fluids produced at the "wet" Nicaraguan subducted mantle (Abers et al., 2003) leads to efficient C extraction from the upper slab sediments. This process would result in larger CO_2 release into the mantle wedge, and could ultimately cause the high CO_2/S_{TOT} ratios in both magmas and gases (Fig. 6). The contrasting more-anhydrous nature of the shallow subducting slab in Costa Rica (Protti et al., 1994) would result in lower C recycling (the C output at the volcanic arc was only 0.15–0.46% of the C input along the slab, compared to a CAVA average of 2% and 3.7–5.1% in Nicaragua; Freundt et al., in press). The resulting low CO_2/S_{TOT} ratios in magmatic gases would therefore result from a dominant contribution of volatiles from the mantle wedge, where a large fraction of the S arc output is typically produced (Wallace, 2005). We admit, however, that underplating of C-rich sediments in Costa Rica possibly plays an additional role.

If the above interpretation is correct, then a positive correlation should be expected between the degree of C enrichment in magmas/gases and petrologic tracers of slab-derived fluids. However, Wehrmann et al. (2011) noted that, while the H_2O contents in MIs are correlated with Ba/La, B/La, and U/Th ratios (Wade et al., 2006; Sadofsky et al., 2008), the CO_2 contents are not directly correlated with the same proxies for a slab-derived component. Although this decoupled behavior of H_2O and CO_2 could partially reflect the influence of the degree of sediment melting (controlled by slab temperature; Plank et al., 2009) on CO_2 recycling (Watt et al., 2013), it must be admitted that pre-entrapment CO_2 degassing, which is likely to have been highest in H_2O-rich Nicaragua magmas, may have complicated (or even obscured) any source-derived trend in MIs. In fact, our inferred magmatic gas CO_2/S_{TOT} ratios are positively correlated with any trace-element proxy for slab-fluids (e.g., Ba/La and U/Th; see Fig. 7c and d), providing additional support for our conclusion that slab-derived fluids are deeply implicated in the generation of CO_2-rich volcanic gases in Nicaragua.

7. Conclusions

Our novel CO_2/S_T ratio and CO_2 output results here contribute to extend the currently incomplete volcanic CO_2 flux data set (Burton et al., 2013). We show that CO_2:S_T compositions of high-temperature volcanic gases – where secondary (scrubbing) processes are insignificant – do vary over relatively restricted ranges (Shinohara, 2013), but still display measurable variations along a volcanic arc. While additional observations over longer measurement intervals are needed to strengthen our conclusions, our data presented here are suggestive of systematic and sizeable differences in volcanic gas signatures between Nicaragua ($CO_2/S_T \sim 3$) and Costa Rica ($CO_2/S_T \sim 0.5$–1.0). This CO_2-richer composition of Nicaraguan gas is consistent with (i) high CO_2 contents recorded in MIs, (ii) the more-positive (e.g., sedimentary) isotopic signatures of N_2 and CO_2 in gas manifestations, and (iii) high values of trace-element proxies for slab-derived fluids in magmas (e.g., high Ba/La, U/Th, and B contents in volcanic rocks). Based on these correlations, we provide additional support for the earlier theory relating CO_2-rich volcanism in Nicaragua to more-efficient C recycling along the "wet" (serpentinized) Nicaraguan slab. We also used our inferred and distinct compositional features for Costa Rica and Nicaragua gases to calculate that the long-term (e.g., based on the magma eruption rate) CO_2 output from the CNVS is ∼3200 tons/day. This geological CO_2 output agrees well with the present-day CO_2 output (2835 ± 1364 tons/day) from the CNVS that we calculated from our gas observations made during March and April 2013.

Evaluating the general significance of along-arc variations in gas chemistry is presently restricted by the limited gas data set available. However, the heterogeneities observed in subduction geometry and conditions worldwide (Syracuse and Abers, 2006) suggest that the gas chemistry can vary substantially both within and between arc segments. Careful identification of the CO_2/S_T-ratio signature of each individual arc segment is key to improving the estimates of volcanic-arc CO_2 outputs at both regional and global scales.

Acknowledgements

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007/2013)/ERC grant agreement n1305377. This study was initiated within the framework of the DECADE initiative of the Deep Carbon Observatory. Tobias Fischer (UNM) kindly provided the portable DOAS used for the Poás walking traverses. Constructive comments by David Hilton and two anonymous reviewers are acknowledged for improving the quality of the manuscript.

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