

Monitoring of temporal and spatial variations in fumarole helium and carbon dioxide characteristics at Poás and Turrialba volcanoes, Costa Rica (2001–2009)

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We report results of a 9-year monitoring program that took place from 2001 to 2009 of the helium and carbon isotope ($^3\text{He}/^4\text{He}$, $\delta^{13}\text{C}$) and relative abundances ratios ($\text{CO}_2/^3\text{He}$) of fumarole sites at Poás and Turrialba volcanoes, Costa Rica. Over the monitoring period, helium isotopes ($^3\text{He}/^4\text{He}$), $\delta^{13}\text{C}_{(\text{CO}_2)}$ and $\text{CO}_2/^3\text{He}$ values varied between 6.7–7.6 R_A (where $R_A = 1.4 \times 10^{-6}$), -5.5 to -1.3‰ (vs. PDB) and 8.2 – 59.5 ($\times 10^9$), respectively, at Poás Volcano. Corresponding values for Turrialba Volcano were 6.9–8.0 R_A , -4.4 to -2.7‰ and 9.4 – 19.6 ($\times 10^9$), respectively. Notably, fumarole sites at both volcanoes underwent changes in temperature, intensity and areal extent during the 9-year period, and Poás Volcano experienced hydrophreatic eruptions and structural damage induced by a nearby earthquake. At both volcanoes, there were significant and sympathetic temporal changes involving all three geochemical parameters—notably in 2001 and 2006 at Poás and in 2001 and between 2005–2007 at Turrialba. We dismiss increased hydrothermal interaction, magma degassing and calcite precipitation as likely causes of the observed variations. Instead, by ascribing endmember compositions to the three principal contributors to the CO_2 inventory—mantle wedge as well as limestone and organic (sedimentary) carbon (both slab and crust derived)—we show that changes in observed He– CO_2 relationships mainly reflect enhanced crustal contributions of CO_2 and increased inputs from magma degassing. Such changes in the relative roles of crust and magma as suppliers of CO_2 are readily apparent in the He– CO_2 temporal record. This work supports calls for long-term geochemical monitoring to be included within hazard assessment and mitigation studies at active volcanoes.

Keywords: helium isotopes, carbon isotopes, Central America, Costa Rica, volcano monitoring

INTRODUCTION

Geochemical monitoring of geothermal fluids at active volcanic systems has provided valuable insight into a variety of subsurface processes. These include magmatic-hydrothermal interactions, degassing behavior of magmatic bodies, geothermal reservoir evolution and earthquake effects (e.g., Oppenheimer *et al.*, 2003; Bundschuh and Alvarado, 2007). Consequently, the large demands in time and personnel required to repeatedly sample the same locations to produce a time-series of observations are often outweighed by gains in scientific understanding. This was our hope in making repeated visits to Poás and Turrialba volcanoes in Costa Rica to collect fumarole samples over a 9-year period starting in 2001.

Poás and Turrialba volcanoes lie on the Central America Volcanic Front and are formed as a consequence of subduction of the Cocos Plate beneath the Caribbean Plate (Carr, 1984; Carr *et al.*, 2003). Both volcanoes are part of the Cordillera Central, one of two Quaternary volcanic ranges in Costa Rica (Alvarado, 1993). There have been numerous time-series studies of lava and gas chemistry variations, particularly at Poás Volcano (e.g., Prosser and Carr, 1987; Rowe *et al.*, 1992; Martínez *et al.*, 2000; Vaselli *et al.*, 2003). Fortuitously, over the course of our monitoring period, both volcanoes experienced significant changes in fumarole characteristics (temperature, intensity and areal extent) and eruptive behavior, providing us with the opportunity to assess the effects of this activity on the He– CO_2 volatile systematics of the fumaroles.

In this contribution, we report the He and CO_2 record—*isotope variations and relative abundance characteristics*—for three fumarole sites at Poás and Turrialba from 2001 to 2009. Although the time-series is discontinuous, we show here that there were significant varia-

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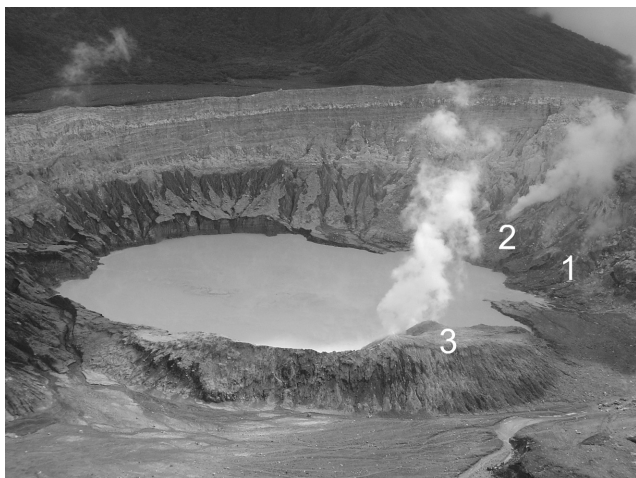


Fig. 1. Location of sampling localities within Poás crater. View to the north from the lookout at the National Park. 1, location of sampling at 2003 IAVCEI Gas Chemistry workshop; 2, Naranja Fumarole; 3, Dome. Photo: 2007 (D. Hilton).



Fig. 2. Location of sampling sites at Turrialba Volcano. View towards the west. 1, West Crater; 2, West Crater (outer wall); 3, Central Crater. Photo: 2007 (E. Füre).

tions in helium and carbon isotope values and in the relative abundances of the two gases over the monitoring period. We suggest that these changes mainly reflect variations in the provenance of the CO₂ which may be degassed from differing parts of the magmatic system which, in turn, have undergone varying degrees of crustal interaction. Such inferences are not possible through single site visits alone. Our studies at Poás and Turrialba attest to the benefits of initiating and maintaining routine monitoring programs at active and sensitive volcanoes over extended periods of time.

SAMPLING STRATEGY AND LOCATIONS

Our monitoring program started at both Poás and Turrialba volcanoes in January, 2001 with further visits taking place in March and July of the same year. The He and CO₂ results from all three sampling visits were published by Shaw *et al.* (2003) in a study aimed at quantifying the efficiency of CO₂ recycling between the Middle America Trench and the Costa Rica-Nicaragua segment of the Central America Volcanic Front. Continuing studies in Costa Rica, and other regions of Central America, gave us opportunities to return to Poás an additional eight times for sampling and to Turrialba three more times, with the last visit being in January, 2009.

At Poás Volcano, we sampled fumarole fields at three different locations on the crater floor. The most continuous record (2001–2007) was obtained from the fumarole field located at the base of the inner crater wall on the eastern side of the crater (Site 1). Starting in 2005, we sampled Naranja fumarole (Site 2) which is found fur-

ther north along the eastern wall of the crater. For the last two visits, we targeted fumaroles located at or near the base of the prominent dome, next to the southern edge of the crater lake (Site 3). Figure 1 shows the approximate location of all three sampling sites.

Sampling at Turrialba Volcano took place at two sites: the West Crater (Sites 1 and 2) and the Central Crater (Site 3)—see Fig. 2. Various fumaroles located on the main crater wall, adjacent to the West Crater, were sampled in 2001 (Site 1) whereas the outer wall of the West Crater was sampled in 2009 (Site 2). Fumaroles at or close to the Central Crater were sampled in odd numbered years from 2005 onwards. The two craters are about 500 meters apart. Starting in June, 2005, the level of fumarolic activity in the West Crater increased markedly, leading to extensive areas of vegetation kills. This activity continues in both the West and Central craters (as of January, 2010).

It should be noted that significant changes occurred at the various fumaroles fields over the course of the monitoring period. These changes included fumaroles becoming more/less vigorous as well as fumarole temperatures increasing/decreasing. There were also changes in the area of fumarolic activity at some sites. A more detailed account of these changes, occurring at both Poás and Turrialba, can be found on-line in reports of the Bulletin of the Global Volcanism Network (2001–2009) (see: www.volcano.si.edu). We emphasize, however, that we endeavored to maintain integrity and continuity of the sampling record by targeting either the same fumaroles or fumaroles as close as possible to the location of fumaroles sampled previously.

SEISMIC AND VOLCANIC ACTIVITY

Details of seismic and volcanic activity at Poás and Turrialba volcanoes can be found at the archives of the Global Volcanology Program (GVP) and are also readily accessible on-line (www.volcano.si.edu). These archives include both official and individual reports. Here, we describe the main changes that occurred at both volcanoes over the monitoring period.

Briefly, the period 2001–2009 showed marked changes at both Poás and Turrialba volcanoes. The early part of the monitoring period at Poás was characterized by a generally low level of seismicity but with some changes in the level of fumarolic activity, the occurrence of occasional mass wasting events and variations in the water level, temperature and pH of the crater lake. In March, 2006, however, there was a series of small phreatic eruptions from the crater lake with the ejection of water, blocks and sediment. These eruptions were accompanied by seismic tremor events. Further phreatic eruptions occurred in September, 2006 with ejection of some material to a height of over 350 meters: this was sufficiently powerful that some material was ejected over the western crater wall. More phreatic eruptions from the lake took place in January, 2008 with material erupted to a height of ~200 meters. The most intense seismic activity of the entire monitoring period occurred on January 8th, 2009 when a $M = 6.2$ earthquake struck ~ 10 km to the east of the crater. This event caused significant landslides within the crater and intense fumarolic activity returned to the dome area. Fortunately, samples were collected a few hours before this event.

Seismicity at Turrialba Volcano started to increase in 1996 and reached a maximum of >9000 events/year in 2001. Since that time, the seismic level has remained elevated but significantly lower than the maximum of 2001. The 2001–2006 period also saw increased fumarole activity in the Central Crater with significant impacts on local vegetation. Fumarole activity also increased in the West Crater starting in 2005. By the summer of 2007, new fractures appeared at the summit accompanied by enhanced fumarolic activity including the deposition of native sulfur. Micro-seismicity also increased from this time.

ANALYTICAL APPROACH

All samples from both volcanoes were collected in evacuated 1720-glass flasks. Standard collection procedures were adopted to minimize the possible contamination of samples by air (Hilton *et al.*, 2002). In the laboratory, the samples were prepared for analysis using instrumentation and protocols described previously (e.g., Shaw *et al.*, 2003; De Leeuw *et al.*, 2007). Briefly, all samples

were extracted on a dedicated preparation line with a fraction of the non-condensable gas (containing He and Ne) captured in a 1720-glass breakseal. All the CO₂ was condensed into a Pyrex breakseal following separation from water vapor, active gases (N₂, CO, CH₄) and heavy noble gases (Ar, Kr and Xe).

Helium and neon analyses were carried out on a MAP-215 noble gas mass spectrometer. First, the gas was released from the breakseal and prepared for analysis using a series of traps, held at liquid nitrogen temperature, and active-gas getters. Helium was separated from neon using a helium-cooled refrigeration stage interfaced to a trap lined with activated charcoal. All sample ³He/⁴He ratios were normalized to standard aliquots of air processed and analyzed under identical conditions.

Carbon dioxide was purified on a dedicated line using a variable temperature trap designed to separate CO₂ from sulfur-bearing species. Following clean-up, the amount of CO₂ was measured using a capacitance gauge manometer in a calibrated volume, prior to freezing an aliquot of the CO₂ in a Pyrex breakseal. For isotope analysis, the CO₂ aliquot was inlet into a VG Prism stable isotope mass spectrometer (for samples collected prior to 2007) or a Thermo-Finnigan Delta XP^{Plus} Isotope Ratio Mass Spectrometer (for samples collected in 2007 and later).

RESULTS

All results obtained on samples collected at Poás Volcano are reported in Table 1. Table 2 gives all data for samples collected at Turrialba volcano. Helium isotope results (³He/⁴He) are reported in the R/R_A notation where R = sample ³He/⁴He and R_A = air ³He/⁴He (=1.4 × 10⁻⁶). The air-normalized He/Ne ratio is multiplied by a factor 1.22 which represents the ratio of the Bunsen solubility coefficients of Ne to He at 15°C (Ozima and Podosek, 2002). The resulting value (X) is given in column 6 of Tables 1 and 2. It is used to estimate the air-corrected ³He/⁴He ratio (R_C) of the sample (see Hilton, 1996). As X-values are high for the majority of samples of this study, the correction factor is small and hence there is little difference between measured and corrected ³He/⁴He ratios. The relative abundance of He to CO₂ is reported as the CO₂/³He ratio with the isotopic composition of the carbon (¹³C/¹²C) given in the delta notation (δ¹³C) as the per mil deviation from the PDB standard.

In the following description of results, we include data reported previously for the 2001 sampling campaign (Shaw *et al.*, 2003). In addition, we point out that while duplicate samples generally show good agreement in all three monitored parameters (³He/⁴He, δ¹³C and CO₂/³He), there are exceptions—notably duplicates collected in March, 2001 (Site 1, Poás), February, 2007 (Site 2, Poás)

Table 1. Temporal record of helium and carbon isotope and relative abundance relationships at Poás volcano, Costa Rica

Sampling locality	Sample ID	Date of sampling	Temp. (°C)	(R/R _A) _m ⁽¹⁾	X ⁽²⁾	(R/R _A) _c ^{(3),(4)}	CO ₂ / ³ He ⁽⁴⁾ (×10 ⁹)	δ ¹³ C ⁽⁴⁾ (‰ PDB)	(L+S) ⁽⁵⁾ /M	L/S
Site 1 - Workshop location (N10°11'53.0"; W84°13'43.1")	CR-8	01/2001*	76	7.10	1670	7.10 ± 0.1	15.9 ± 0.8	-5.6	9.6	2.2
	CR-9 (dup)			6.90	1186	6.90 ± 0.1	15.4 ± 0.8	—		
	CR2-6	03/2001*	92	7.21	1190	7.22 ± 0.1	12.4 ± 0.7	—		
	CR2-14 (dup)			7.56	469	7.60 ± 0.1	9.9 ± 0.5	-6.8	5.6	1.7
	CR3-17	07/2001*	93	7.12	440	7.14 ± 0.1	15.3 ± 0.8	-5.8	9.2	2.1
	Poas 3	03/2003	98	7.07	91.3	7.14 ± 0.1	20.3 ± 0.3	-3.5		
	Poas 5			7.15	596	7.16 ± 0.1	24.0 ± 0.4	-3.5	15.0	3.6
	CR-09	06/2005	220	6.90	274	6.92 ± 0.1	26.3 ± 0.8	-1.3	16.6	7.4
	Costa-1	02/2006	113	7.14	488	7.15 ± 0.1	20.4 ± 0.3	-2.4		
	Costa-2 (dup)			7.25	576	7.26 ± 0.1	22.9 ± 0.3	-2.5	14.3	4.8
	Cost-4	11/2006	113	6.44	28	6.64 ± 0.1	47.2 ± 0.8	-2.2	30.6	5.1
	CR-4	02/2007	115	7.12	386	7.13 ± 0.2	16.4 ± 1	-4.9	10.0	2.6
CR07-05	06/2007	115	6.99	475	7.01 ± 0.3	17.8 ± 1.9	-3.5	10.9	3.7	
Site 2 - Naranja Fumarole (N10°12'00.4"; W84°13'51.4")	Poas	06/2005	250	7.20	2734	7.20 ± 0.4	—	—		
	Costa-6	02/2006	153	6.96	1133	6.96 ± 0.1	17.4 ± 0.3	-1.8		
	Costa-7 (dup)			7.11	271	7.14 ± 0.1	23.3 ± 0.3	-1.5	14.6	6.8
	Cost-1	11/2006	97	6.93	76	7.01 ± 0.3	59.5 ± 1.7	—		
	CR-1	02/2007	115	6.55	42	6.66 ± 0.2	16.1 ± 1	-4.2		
	CR-3 (dup)			6.96	136	7.00 ± 0.2	18.2 ± 1.2	-2.8	11.2	4.5
	CR07-02	06/2007	117	7.24	116	7.29 ± 0.3	20.3 ± 2.2	-3.8	12.6	3.4
	CR07-03 (dup)			7.16	225	7.18 ± 0.3	19.7 ± 2.1	-3.6		
	CR08-07	03/2008	93	6.79	27	7.01 ± 0.1	14.9 ± 0.4	-3.8	9.0	3.4
Site 3 - Base of Dome (N10°11'47.6"; W84°13'48.1")	CR08-04	03/2008	93	7.06	215	7.09 ± 0.1	11.0 ± 0.3	-2.8	6.3	4.8
	CR08-05 (dup)			7.04	228	7.06 ± 0.1	20.0 ± 0.5	-2.5		
	CR01/09-03	01/2009	93	7.19	103	7.24 ± 0.1	—	—		
	CR01/09-11 (dup)			7.37	138	7.40 ± 0.7	—	—		

Dashed line (—) indicates “not determined”.

n.a. = Not available.

Asterisk (*) denotes dates of sampling reported in Shaw et al. (2003)—2001 data only.

⁽¹⁾R_m/R_A is the measured ³He/⁴He ratio divided by the ³He/⁴He in air = 1.4 × 10⁻⁶.

⁽²⁾X = (⁴He/²⁰Ne)_{measured}/(⁴He/²⁰Ne)_{air} × βNe/βHe and β represents the Bunsen coefficients from Weiss (1971) assuming a groundwater recharge temperature of 15 °C.

⁽³⁾R_C/R_A is the air-corrected He isotope ratio = [(R_m/R_A × X) - 1]/(X - 1).

⁽⁴⁾All errors are reported at the 1σ level, δ¹³C errors are ±0.3‰.

⁽⁵⁾L, S and M represent CO₂ of limestone, sedimentary organic and mantle origin, respectively (see text for explanation).

and July, 2001 (Site 1, Turrialba). In each of these cases, we include in the discussion only the results of the duplicate sample with the highest air-corrected ³He/⁴He value (R_C)—the assumption being that there is a greater degree of uncertainty associated with data of the sample having the lower R_C/R_A value.

Helium isotopes

The air-corrected ³He/⁴He ratio (R_C) at Poás volcano falls between a maximum value of 7.6 R_A (Site 1; March 2001) and a minimum ratio of 6.7 R_A (Site 2; February 2007). Thus, helium is predominantly of mantle origin with evidence of a small but discernible addition of radiogenic helium at all locations. In a two-component mixture of MORB-like He (8 R_A; Graham, 2002) and radio-

genic He (0.05 R_A; Andrews, 1985) the proportion of mantle helium at Poás varies between 95 and 84%.

There is little evidence of a significant difference in ³He/⁴He ratios between the three sampling sites within Poás crater. The mean (±one standard deviation) air-corrected ³He/⁴He ratio (R_C) at Site 1 (7.12 ± 0.26; n = 9), Site 2 (7.11 ± 0.12; n = 6), and Site 3 (7.25 ± 0.22; n = 2) is identical within error. This approach assumes all samples are drawn from the same population—an assumption that may not necessarily be true if the isotopic composition of He reflects different mixtures of magmatic and radiogenic helium.

At Turrialba, the maximum and minimum air-corrected ³He/⁴He ratios are 8.0 R_A (Site 1; March, 2001) and 6.9 R_A (Site 3; June, 2005), respectively. In this instance, the

Table 2. Temporal record of helium and carbon isotope and relative abundance relationships at Turrialba volcano, Costa Rica

Sampling locality	Sample ID	Date of sampling	Temp. (°C)	(R/R _A) _m ⁽¹⁾	X ⁽²⁾	(R/R _A) _c ^{(3),(4)}	CO ₂ / ³ He ⁽⁴⁾ (×10 ⁹)	δ ¹³ C ⁽⁴⁾ (‰ PDB)	(L+S) ⁽⁵⁾ /M	L/S
Site 1 - West Crater N10°01'09.4"; W83°45'56.2"	CR-2	01/2001*	90	—	—	—	—	−3.3		
	CR-3 (dup)			7.73	671	7.74 ± 0.07	14.3 ± 0.7	−4.1	8.6	3.2
	CR2-1	03/2001*	90	8.10	602	8.01 ± 0.1	9.8 ± 0.5	−4.4		
	CR2-2 (dup)			8.10	979	8.01 ± 0.1	9.4 ± 0.5	−3.8	5.3	3.6
	CR3-2	07/2001*	84	7.69	565	7.70 ± 0.07	16.1 ± 0.8	−4.2	9.8	3.1
Site 2 - West Crater (outer wall) N10°01'09.1"; W83°45'49.9"	CR01/09-16	01/2009	92	7.68	1757	7.68 ± 0.2	—	—		
Site 3 - Central Crater N10°01'14.4"; W83°45'47.1"	CR-14	06/2005	88	6.52	17.1	6.86 ± 0.2	19.6 ± 1	−2.7	12.1	4.6
	CR-12 (dup)			6.53	17.9	6.85 ± 0.2	18.4 ± 1	−2.7		
	CR-09	06/2007	88	7.44	417	7.48 ± 0.3	12.5 ± 1	−3.8	7.3	3.5
	CR01/09-13	01/2009	89	7.09	2742	7.09 ± 0.2	—	—		

Dashed line (—) indicates “not determined”.

Asterik (*) denotes dates of sampling reported in Shaw et al. (2003)—2001 data only.

⁽¹⁾R_m/R_A is the measured ³He/⁴He ratio divided by the ³He/⁴He in air = 1.4 × 10^{−6}.

⁽²⁾X = (⁴He/²⁰Ne)_{measured}/⁴He/²⁰Ne_{air} × βNe/βHe and β represents the Bunsen coefficients from Weiss (1971) assuming a groundwater recharge temperature of 15 °C.

⁽³⁾R_c/R_A is the air-corrected He isotope ratio = [(R_m/R_A × X) − 1]/(X − 1).

⁽⁴⁾All errors are reported at the 1σ level, δ¹³C errors are ±0.3‰.

⁽⁵⁾L, S and M represent CO₂ of limestone, sedimentary organic and mantle origin, respectively (see text for explanation).

mantle-derived component varies from 100–86% assuming the same endmember ³He/⁴He values as above. A noticeable difference in the case of Turrialba is that there is a significant difference in ³He/⁴He ratios between the two sampling localities. The West Crater (Sites 1 and 2) has an average ³He/⁴He value over the monitoring period of 7.78 R_A (±0.15; n = 4) whereas the average value for the Central Crater (Site 3) is lower at 7.14 R_A (±0.31; n = 3). These results are consistent with a greater contribution of crustal helium at the site of the Central Crater.

Carbon isotopes

The carbon isotope record at Poás Volcano shows significant variability—with a difference of 5.5‰ found at one site (Site 1). The highest δ¹³C value was recorded in June, 2005 (−1.3‰) and the lowest was −6.8‰ in March, 2001. The average value of δ¹³C found at this site is −4.0 ± 1.9‰ (n = 9) so the extreme values fall outside the one sigma uncertainty envelope. However, there is no evidence (within error) for a difference in δ¹³C between sites: Site 2 (Naranja fumaroles) has a mean δ¹³C value of −3.0 ± 1.1‰ (n = 4), and the sole value for Site 3 (Dome) is −2.8‰, again falling within the range of the error estimate for Site 1.

The absolute δ¹³C values at Turrialba are similar to those found at Poás. The Central Crater (Site 3) is characterized by a mean δ¹³C value of −3.3 ± 0.8‰ (n = 2) whereas the West Crater (Sites 1 and 2) has a slightly lower value of −4.0 ± 0.2‰ (n = 3).

CO₂/³He ratios

The relative proportions of CO₂ and He (given as the CO₂/³He value) fall within the range 8.2–59.5 (×10⁹) at Poás. Therefore, all values are significantly greater than the value usually associated with MORB-mantle (~2 × 10⁹; Marty and Jambon, 1987). This range is consistent with the addition of CO₂—from either the subducting Cocos Plate or as crustal contamination from the overriding Caribbean Plate—to mantle-wedge derived carbon. Within the crater of Poás, there is little difference in the mean values of CO₂/³He (×10⁹) at Site 1 (21.7 ± 11) and Site 2 (25.6 ± 17).

There is also good agreement in CO₂/³He between the two craters at Turrialba Volcano although the absolute values are slightly lower than at Poás. At the West Crater (Sites 1 and 2), the CO₂/³He ratio is 13.3 ± 3 (×10⁹) whereas it is 16.1 ± 5 (×10⁹) at the Central Crater. Again, the values are similar to that found at other subduction-related volcanoes worldwide (Sano and Williams, 1996).

DISCUSSION

There are a number of potential processes that could contribute to the variations observed in the three monitored parameters of this study. In the next section (Subsection “Controls on variations in ³He/⁴He, δ¹³C and CO₂/³He values”), we evaluate near-surface or shallow processes which can act to fractionate He and CO₂ and modify δ¹³C values. In the following two sections, we assess the

temporal record of (a) He–CO₂ variations (Subsection “Temporal variations in ³He/⁴He, δ¹³C and CO₂/³He values”), and (b) the modeled provenance of CO₂ (Subsection “Temporal variations in modeled parameters: L-M-S components”), and show how they lead to the identification of crust-mantle interaction as the main control on the variations observed at both Poás and Turrialba volcanoes (Subsection “Crustal versus mantle volatiles”).

Controls on variations in ³He/⁴He, δ¹³C and CO₂/³He values

Near surface interactions within hydrothermal systems have the potential to affect He–CO₂ relationships (e.g., Ray *et al.*, 2009). At Poás, there is an extensive near-surface hydrothermal system, which interacts with the acid crater lake (Rowe *et al.*, 1992). The observation that the majority of samples have high ³He/⁴He (this study) with prior work showing low temperature fumaroles at Poás having C/S ratios > 1 (Zimmer *et al.*, 2004) points to extensive interaction between volatiles of deep-seated (magmatic) origin and the shallow aqueous system. Indeed, it is the hydrothermal system which acts to transfer the magmatic volatiles to the atmosphere via fumaroles on the lake shore. We anticipate that any increased shallow-level interaction with the crater lake over the course of the monitoring period would be manifested in lowering of fumarole CO₂/³He values, due to higher solubility of CO₂ in the water phase (Wilhelm *et al.*, 1977), accompanied by a decrease in temperature. There is scant evidence of such trends at Poás or Turrialba volcanoes (Tables 1 and 2). For example, the gradual increase in temperature at Site 1 at Poás observed over the course of the monitoring period is not accompanied by an increase in CO₂/³He values. Even the observation of molten sulfur at Site 1 and corresponding spike in temperature in June, 2005 did not affect the CO₂/³He value significantly. Likewise, there is no obvious correlation at the Naranja fumarole (Site 2, Poás). At Turrialba, CO₂/³He values vary by a factor of two, yet temperature fluctuations are muted and fall within 6°C. Thus, we conclude that observed variations in He–CO₂ are not influenced to any great extent by hydrothermal interaction.

Another obvious process that may affect monitored He–CO₂ values is magmatic degassing, in which case, gas loss from a magmatic body would produce large and discernible trends in both CO₂/³He and δ¹³C values. Such trends depend upon the mode (open vs. closed system) and extent of gas loss, and would result in a decrease in CO₂/³He and δ¹³C for magma of tholeiitic composition. Using fractionation factors of 2.35 and –4‰ respectively (see discussion Ray *et al.*, 2009), CO₂/³He and δ¹³C values at Poás Volcano would decrease from starting values of 47.2 × 10⁹ and –2.2‰ (highest values at Site 1) to 20.1 × 10⁹ and –6.2‰ in closed system mode. In the case of

open-system or Rayleigh degassing, δ¹³C would fall to –13‰ as the residual CO₂/³He value decreased to 9.9 × 10⁹ (the lowest measured value at Site 1). By considering both the absolute values of the measured parameters and changes compared to the previous sampling period (Tables 1 and 2), there are no indications for degassing control on the He–CO₂ systematics of either volcano by closed or open system gas loss.

Finally, other possible controls on the He–CO₂ systematics include calcite precipitation within the hydrothermal system which can act to decrease CO₂/³He values and modify δ¹³C ratios depending upon the temperature (see Ray *et al.*, 2009). Evaluation of this possibility is difficult without detailed gas/fluid geothermometry but we note that if temperatures of the hydrothermal system at Poás are close to boiling point, loss of CO₂ should be accompanied by a discernible decrease in δ¹³C of the gaseous CO₂. Again, we point out that variations in δ¹³C at all our monitored localities cover a restricted range only so that while we cannot dismiss this possibility, it must be regarded as remote.

We now turn our attention to the temporal variability in ³He/⁴He, δ¹³C and CO₂/³He and consider if changes in the source or provenance of the volatiles can account for the observed variations. In particular, we focus on the two obvious sources of volatiles in the active volcanic systems of Poás and Turrialba, namely mantle-derived volatiles characteristic of magmatic intrusions within the system and crustal volatiles that may be added to the system by assimilation, stoping or any other mechanism associated with crust-magma interaction.

Temporal variations in ³He/⁴He, δ¹³C and CO₂/³He values

The temporal record of the three parameters monitored as part of this study (³He/⁴He, δ¹³C and CO₂/³He) for Poás Volcano is plotted in Fig. 3. The figure includes data from all three sites in the crater. Also plotted are the times of the phreatic eruptions of 2006 and 2008 as well as the timing of the earthquake in January, 2009.

There are a number of features of the Poás record that merit comment. In the first instance, we are interested in whether changes occur for only one of the monitored parameters or if three parameters change simultaneously. Additionally, we make a note if there is a relationship between the occurrence of seismic/volcanic activity and changes in He and/or CO₂ characteristics. We point out the following four features of the Poás record (which are labeled on Fig. 3):

1. There is a discernible increase in ³He/⁴He at Site 1 in March, 2001 relative to adjacent sampling times of January and July, 2001. The increase in ³He/⁴He is accompanied by a sympathetic decrease in both δ¹³C and CO₂/³He. There were no hydrophreatic eruptions or any

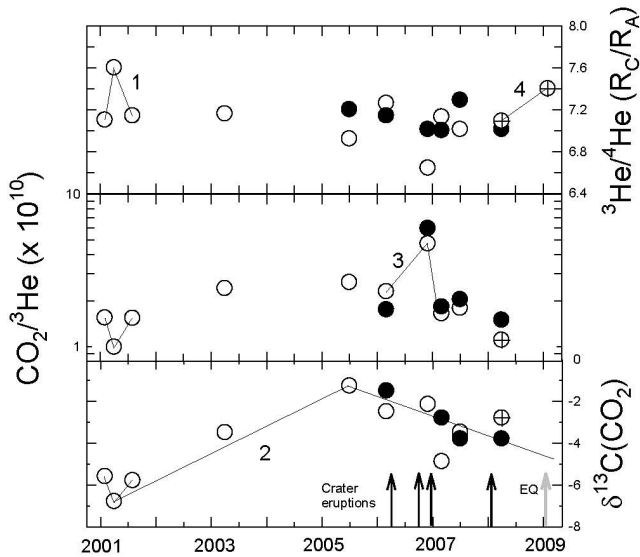


Fig. 3. Temporal variations in ${}^3\text{He}/{}^4\text{He}$ (R_C/R_A), $\text{CO}_2/{}^3\text{He}$ and $\delta^{13}\text{C}$ values at Poás Volcano over the time period 2001–2009. Times of crater phreatic eruptions are indicated by black arrows; the time of the $M = 6.2$ earthquake (EQ) in 2009 is plotted as a grey arrow. Symbols: open circles (Site 1), filled circles (Site 2) and crossed circle (Site 3). Numbered lines represent temporal trends in ${}^3\text{He}/{}^4\text{He}$, $\text{CO}_2/{}^3\text{He}$ and/or $\delta^{13}\text{C}$ —see text for discussion.

anomalous seismic events over this time period.

2. There is a steady increase in $\delta^{13}\text{C}$ at Site 1 between January, 2001 and June, 2005. Thereafter, the $\delta^{13}\text{C}$ falls to values observed in 2003. The decrease in $\delta^{13}\text{C}$ at Site 1 (post 2005) is accompanied by a decrease in $\delta^{13}\text{C}$ at Site 2. There is a muted response in the $\text{CO}_2/{}^3\text{He}$ signal which mirrors that of $\delta^{13}\text{C}$. There are no discernible changes in ${}^3\text{He}/{}^4\text{He}$. The inflection point for the $\delta^{13}\text{C}$ trend (June, 2005) occurred at least 9 months before the first phreatic eruption in 2006.

3. A sharp increase in the $\text{CO}_2/{}^3\text{He}$ signal is apparent in November, 2006 at both Site 1 and Site 2. This is accompanied by a decrease in ${}^3\text{He}/{}^4\text{He}$ at Site 1 but not at Site 2. The $\delta^{13}\text{C}$ value at Site 1 increases slightly in November, 2006 compared to values obtained at adjacent (prior and following) sampling times: unfortunately, the $\delta^{13}\text{C}$ value for Site 2 at this time was not determined. A series of small phreatic eruptions occurred in the crater approximately 1 month prior to (late September) and 1 month after (mid December) the changes in He– CO_2 .

4. Sampling of the Dome location (Site 3) a few hours prior to the 2009 earthquake revealed that its ${}^3\text{He}/{}^4\text{He}$ ratio had increased from 7.1 to 7.4 R_A since the previous sampling time of March, 2008. No data was obtained for the other parameters.

The temporal record of Turrialba Volcano is less com-

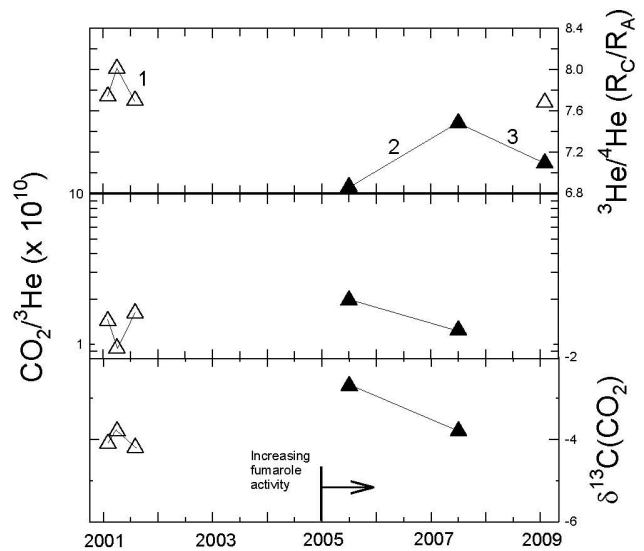


Fig. 4. Temporal variations in ${}^3\text{He}/{}^4\text{He}$ (R_C/R_A), $\text{CO}_2/{}^3\text{He}$ and $\delta^{13}\text{C}$ values at Turrialba Volcano over the time period 2001–2009. Open symbols, Sites 1 and 2 (West Crater); filled symbols, Site 2 (Central Crater). Numbered lines represent temporal trends in ${}^3\text{He}/{}^4\text{He}$, $\text{CO}_2/{}^3\text{He}$ and/or $\delta^{13}\text{C}$ —see text for discussion.

plete than that of Poás (Fig. 4): nevertheless, there are a number of noteworthy points:

1. There is an increase in ${}^3\text{He}/{}^4\text{He}$ in March, 2001 at the West Crater (Site 1) compared to values obtained in January and July, 2001. The same effect is seen at Poás although the volcanoes are >100 km apart. The increase in ${}^3\text{He}/{}^4\text{He}$ at Turrialba is mirrored by an increase in $\delta^{13}\text{C}$ but a decrease in $\text{CO}_2/{}^3\text{He}$. These changes coincided with the observation that the number of earthquakes reached a peak at Turrialba in 2001.

2. There is a marked increase in ${}^3\text{He}/{}^4\text{He}$ at the Central Crater (Site 3) between June, 2005 and the following sampling visit in June, 2007. This change coincided with an increase in fumarolic activity at Turrialba which started in 2005. The change in ${}^3\text{He}/{}^4\text{He}$ is inversely correlated with changes in $\delta^{13}\text{C}$ and $\text{CO}_2/{}^3\text{He}$.

3. Helium isotopes at the Central Crater (Site 2) decreased from a high in 2007 (7.5 R_A) to an intermediate value (7.1 R_A) in 2009. The ${}^3\text{He}/{}^4\text{He}$ ratio at the Central Crater remained low relative to all values obtained for the West Crater (2001 and 2009 data).

In summary, there are a number of instances in the records of both Poás and Turrialba volcanoes where there are simultaneous changes in the isotope characteristics (both ${}^3\text{He}/{}^4\text{He}$ and $\delta^{13}\text{C}$) and relative abundances. Specifically, these are observations 1 and 3 above for Poás and observations 1 and 2 above for Turrialba. The long(er) term change in $\delta^{13}\text{C}$ at Poás (observation 2) is not ac-

accompanied by clear changes in $\text{CO}_2/{}^3\text{He}$ or ${}^3\text{He}/{}^4\text{He}$. Incomplete records for 2009 (Poás—observation 4 and Turrialba—observation 3) preclude further detailed analysis.

Temporal variations in modeled parameters: L-M-S components

The changes in the isotopic composition of CO_2 at Poás and Turrialba coupled with variations in its abundance relative to He are consistent with variations in the provenance (origin) of this major gas species. There are three generally regarded sources of CO_2 at subduction-zone volcanoes—mantle wedge (M), and limestone (L) and organic sediments (S) of the subducting plate (Marty *et al.*, 1989; Sano and Marty, 1995; Sano and Williams, 1996). In addition, the overriding arc crust can also be regarded as a source of CO_2 , although in this case, the L- and S-components are expected to dominate. Thus, there are a number of potential sources that can contribute to the total CO_2 vented at the surface. Changes in the relative proportions of these sources would be expected to be reflected in variations in the measured values of $\delta^{13}\text{C}$ and $\text{CO}_2/{}^3\text{He}$. In the following analysis, therefore, we model the provenance of the CO_2 at Poás and Turrialba using the three endmember compositions cited above, prior to considering if changes reflect processes occurring in the mantle source of the CO_2 versus the near-surface, crustal environment.

The approach used follows closely that adopted in our previously work in Central America (Shaw *et al.*, 2003; De Leeuw *et al.*, 2007). We assume that the mantle wedge (M), limestone (L) and sediments (S) can be characterized by distinctive $\delta^{13}\text{C}$ and $\text{CO}_2/{}^3\text{He}$ characteristics. In order, these are: M ($\delta^{13}\text{C} = -6.5\text{‰}$ and $\text{CO}_2/{}^3\text{He} = 1.5 \times 10^9$), L ($\delta^{13}\text{C} = +1.9\text{‰}$ and $\text{CO}_2/{}^3\text{He} = 1 \times 10^{13}$) and S ($\delta^{13}\text{C} = -22\text{‰}$ and $\text{CO}_2/{}^3\text{He} = 1 \times 10^{13}$)—see De Leeuw *et al.* (2007) for details. Furthermore, we assume that the measured $\delta^{13}\text{C}$ and $\text{CO}_2/{}^3\text{He}$ values reflect the sum of contributions from the three endmember sources, such that the following mass balance equations apply:

$$({}^{13}\text{C}/{}^{12}\text{C})_{\text{O}} = f_{\text{M}}({}^{13}\text{C}/{}^{12}\text{C})_{\text{M}} + f_{\text{L}}({}^{13}\text{C}/{}^{12}\text{C})_{\text{L}} + f_{\text{S}}({}^{13}\text{C}/{}^{12}\text{C})_{\text{S}} \quad (1)$$

$$1/({}^{12}\text{C}/{}^3\text{He})_{\text{O}} = f_{\text{M}}/({}^{12}\text{C}/{}^3\text{He})_{\text{M}} + f_{\text{L}}/({}^{12}\text{C}/{}^3\text{He})_{\text{L}} + f_{\text{S}}/({}^{12}\text{C}/{}^3\text{He})_{\text{S}} \quad (2)$$

$$f_{\text{M}} + f_{\text{L}} + f_{\text{S}} = 1 \quad (3)$$

where “O” stands for observed, and “f” refers to the fraction of component M, L or S.

Under these conditions, we can resolve the provenance of the CO_2 into M-, L- and S-contributions. In Tables 1 and 2, we present these results as (a) the ratio of lime-

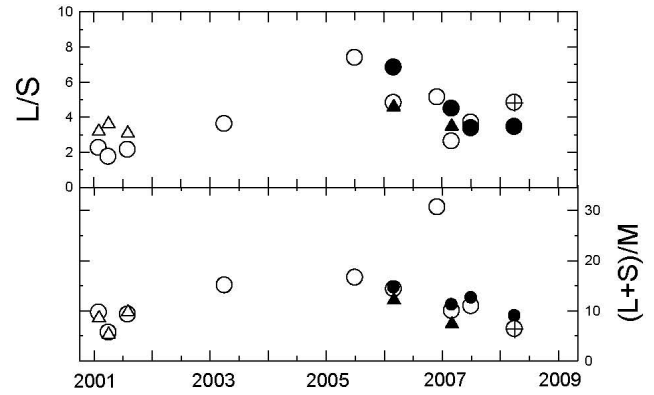


Fig. 5. Temporal variations in the provenance of CO_2 in terms of $(\text{L}+\text{S})/\text{M}$ and L/S (see text for details) at Poás and Turrialba volcanoes over the time period 2001–2009. Symbols as in Figs. 3 and 4.

stone plus sediment to mantle wedge contributions, i.e., $(\text{L}+\text{S})/\text{M}$, and (b) the ratio of limestone to organic sediment contributions (L/S). The temporal record of both these parameters is plotted in Fig. 5.

The temporal variations in $(\text{L}+\text{S})/\text{M}$ and L/S allow us to determine the likely cause(s) behind the observed changes in $\delta^{13}\text{C}$ and $\text{CO}_2/{}^3\text{He}$ at the various monitored sites. Referring to the observed changes in the order listed in the previous section, we note for Poás:

1) March, 2001: Changes at Site 1 reflect an increase in the mantle wedge contribution to the CO_2 inventory. The proportions of L- and S-derived CO_2 remains almost constant.

2) June, 2005: The proportion of L-derived CO_2 increases between 2001 and 2005 and diminishes thereafter. This is reflected in a slight increase in the non-mantle wedge contribution ($\text{L}+\text{S}$).

3) November, 2006: The sharp spike in $\text{CO}_2/{}^3\text{He}$ likely reflects a large increase in the non-mantle wedge contribution ($\text{L}+\text{S}$).

In the case of Turrialba:

1) March, 2001: The sharp decrease in $\text{CO}_2/{}^3\text{He}$ likely reflects an increase in the mantle wedge contribution to the CO_2 inventory.

2) June 2005–June, 2007: These changes are consistent with both a decrease in L/S and $(\text{L}+\text{S})/\text{M}$, i.e., a decrease in the relative L-contribution at the expense of an increase in the M-contribution.

These observations can be summarized by noting that in three cases (observation 1 at Poás and both observations at Turrialba), the observed changes reflect an increase in the relative proportion of mantle-derived CO_2 . The latter two changes at Poás (between 2001 and 2005, and November, 2006) were caused by a relative increase in the non-mantle, particularly the L-derived component.

The question that now arises is whether these changes reflect processes occurring in the mantle wedge, and thereby trace subduction zone effects, or if crust-mantle interaction and crustal contamination are the principal controls.

Crustal versus mantle volatiles

Prior work on the He–CO₂ systematics of Costa Rica and other Central America volcanoes adopted a screening filter to help ensure that only mantle-derived volatiles are considered and resolved into component structures (Shaw *et al.*, 2003; De Leeuw *et al.*, 2007). This process involves selecting only geothermal samples with ³He/⁴He ratios that fall within the MORB-range ($8 \pm 1 R_A$; Graham, 2002), with the implicit assumption that crustal volatiles—characterized by lower ³He/⁴He ratios—are absent. In this way, the provenance of L- and S-components can be ascribed to the down-going slab and be used to trace recycling of CO₂ to the surface. However, the possibility exists that the crust of the overriding plate (the Caribbean Plate in this case) can release carbon—if present in crustal lithologies—as a result of interaction with mantle-derived melts. This has been clearly seen at geothermal localities and volcanic systems sited on thickened crust (e.g., Chile; Ray *et al.*, 2009). The anticipated signal of such crustal interaction is that ³He/⁴He would be expected to be lowered due to release of radiogenic helium produced *in-situ* in crustal rocks. Under these circumstances, some of the CO₂ is also likely to have an origin in the crust.

The changes in the He–CO₂ record at Poás up to June, 2005 and in November, 2006 provide a means to test this hypothesis. Both periods involved an increase in the proportion of CO₂ derived from (L+S) sources. If indeed this increase has a crustal origin then the ³He/⁴He ratios of these samples would be expected to decrease.

As can be observed in Fig. 3, the ³He/⁴He ratio at Site 1 in Poás decreases from a high of 7.6 R_A (March, 2001) through 7.2 R_A (June, 2003) to 6.9 R_A (June, 2005). Thereafter, it is higher at all times except November, 2006. Therefore, there seems to be an inverse correlation between ³He/⁴He ratios at this locality and the proportion of CO₂ derived from the L+S components. This relationship is consistent with a crustal origin for at least a proportion of the non-mantle CO₂.

It is also informative to consider the ³He/⁴He ratios prior to and following the large spike in (L+S)/M ratio of November, 2006. The ³He/⁴He value in February, 2006 was 7.3 R_A whereas it decreased to 6.6 R_A in November before returning to an intermediate value of 7.1 R_A in February, 2007. The same inverse correlation between ³He/⁴He and (L+S)-derived CO₂ is evident. Both these instances suggest that there is an increased contribution of crustal-liberated CO₂ to that transferred from depth

via mantle-derived melts. Interestingly, the phreatic eruptions that have characterized Poás in recent years (Fig. 3) have all occurred after June, 2005. Whether increased crustal interaction with mantle-derived melts has contributed to the eruptive activity remains an open question.

Finally, we consider the 3 instances when the proportion of mantle-derived CO₂ has increased (March, 2001 at Poás and Turrialba, and from June, 2005 to June, 2007 at Turrialba). Circumstances that might lead to an increase in the proportion of mantle-derived CO₂ would be release of volatiles from mantle-derived magma which had undergone minimal or negligible wall-rock interaction with crust. In this case, ³He/⁴He ratios could be expected to increase relative to adjacent sampling times. This is clearly the case in March, 2001 at Poás and Turrialba—maximum ³He/⁴He ratios of 7.6 R_A and 8.0 R_A, respectively, were recorded for the March, 2007 sampling period compared to results for either the preceding January or July periods. The same observation characterizes ³He/⁴He ratios at Turrialba from 2005 to 2007—values increased from 6.9 R_A to 7.5 R_A in the Central Crater (Site 2) as the proportion of mantle-derived CO₂ increased from 7.6 to 12.0%. This time period was marked by a dramatic increase in fumarolic activity at Turrialba, leading to extensive vegetation damage, and continuing high levels of seismicity. The He–CO₂ record over this period is consistent with volatile release from previously un-tapped or new magmatic intrusions or magmas recently intruded to high levels in the crust.

CONCLUDING REMARKS

Our monitoring program at Poás and Turrialba has revealed new insights into the behavior of He and CO₂ at active volcanoes. Both the isotopic characteristics of these two volatiles and their relative abundance characteristics are seen to vary over short time-scales of months-to-years. Such changes are ascribed to variations in the degree of crust-mantle interaction of magmatic bodies—ultimately derived from the mantle wedge and produced in response to plate convergence. Poás and Turrialba remain active and surrounding areas continue to be prone to eruptive and seismic disruption. Helium and CO₂ collected in fumarolic emissions provide clues to sub-surface processes involving magma intrusion, movement, degassing and crustal interaction. Their use as geochemical tracers, as in the present context, can only further understanding of natural hazards in Central America.

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GINs program (NSF) and The Commission on the Chemistry of Volcanic Gases (IAVCEI) hosted workshops in San Jose/Heredia in 2001, 2003 and 2007—all 3 workshops gave us the opportunity to continue our monitoring efforts. Other visits to Poás and Turrialba were supported by laboratory funds from SIO and UNM. Martin Wahlen and Bruce Deck (SIO) are thanked for help with carbon isotope analyses. Antonio Paonita and Yuri Taran provided helpful and constructive reviews.

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