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Diffuse CO_2 degassing and volcanic activity at Cape Verde islands, West Africa

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Abstract

Diffuse CO_2 emission surveys were carried out at São Vicente, Brava, and Fogo islands, Cape Verde, archipelago to investigate the relationship between diffuse CO_2 degassing and volcanic activity. Total amounts of diffuse CO_2 discharged through the surface environment of the islands of São Vicente, Brava, and Fogo were estimated in 226, 50, and 828 t d^{-1}, respectively. The highest CO_2 efflux values of the three volcanic islands systems were observed at the summit crater of Pico do Fogo (up to 15.7 kg m^{-2} d^{-1}). Statistical graphical analysis of the data suggests two geochemical populations for the diffuse CO_2 emission surveys. The geometric mean of the peak population, expressed as a multiple of the geometric mean of the background population, seems to be the best diffuse CO_2 emission geochemical parameter to correlate with the volcanic activity (age of the volcanism) for these three island volcanic systems at Cape Verde. This observation is also supported by helium isotopic signature observed in the Cape Verde's fluids, fumaroles, and ground waters. This study provides useful information about the relationship between diffuse CO_2 degassing and volcanic activity at Cape Verde enhancing the use of diffuse CO_2 emission as a good geochemical tool, for volcanic monitoring at Cape Verde as well as other similar volcanic systems.

Keywords: Diffuse CO_2 emission; Volcanic activity; Cape Verde

Background

Gases emitted from a volcano are usually released as visible emanations from the main crater areas (as plumes and fumaroles) as well as through the surface of the volcano as diffuse degassing. This last type of degassing can be as important as visible emissions (Baubron et al. 1990; Allard et al. 1991; Chiodini et al. 1996; Hernández et al. 1998, 2001a, 2003, 2012b; Gerlach et al. 2001; Rogie et al. 2001; Salazar et al. 2001; Pérez et al. 2004, 2013; Padrón et al. 2008). Among volcanic gases, CO_2 is widely used in volcano gas studies and monitoring because it is one of the first gas species released from ascending magma, and it is considered conservative (Gerlach 1986). The study of diffuse CO_2 degassing is important for gas budgets of volcanoes (Burton et al. 2013; Hards 2005; Pérez et al. 2011) and for monitoring volcanic activity, since the large emissions of CO_2 into the atmosphere (Gerlach et al. 2001; Hernández et al. 2001a; Granieri et al. 2006; Arpa et al. 2013; Pérez et al. 2013; Melián et al. 2014) as well as changes in the temporal evolution of CO_2 efflux (Salazar et al. 2002; Carapezza et al. 2004, 2012; Pérez et al. 2006, 2012; Liuzzo et al. 2013; De Gregorio et al. 2014; Padilla et al. 2014) can be correlated with volcanic activity.

Efforts have been made to obtain a CO_2 flux baseline for a given volcanic system (Salazar et al. 2001). However, very few studies have been focused on investigating the relationship between the magnitude of diffuse CO_2 emissions and volcanic activity (eruptive recurrence) at different volcanic systems in similar geological setting (i.e., volcanic islands that belong to the same archipelago). Notsu et al. (2006) proposed a five-stage evolutionary model for the release of volcanic gas based on the relationship between level of volcanic activity and degassing pattern (diffuse vs. plume CO_2 emission). This model represents an important approach to estimate both visible and non-visible emissions from different volcanoes in a similar state of activity. Williams-Jones et al. (2000) investigated the diffuse degassing (radon and CO_2) at three

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subduction-related volcanoes: Poás and Arenal in Costa Rica and Galeras in Colombia. Although they found that fracturing, hydrothermal development and regional structure are the main variables that may affect flank degassing; this study was carried out at volcanoes with similar level of volcanic activity (all of them exhibiting plume emission and with frequent eruption episodes). The main purpose of this study is to investigate first the relationship between diffuse CO_2 degassing and volcanoes of the Cape Verde, a hot spot archipelago (Holm et al. 2006), with different levels of volcanic activity in the same geological setting. To do this, we have performed a soil gas study at three different volcanic systems: São Vicente, Brava, and Fogo islands, which belong to different geological epochs, aimed at (1) quantifying the rate at which CO_2 is diffusely degassed from the three volcanic islands, (2) identifying and defining the structures controlling the degassing process, and (3) investigating of the relationship between volcanic activity and diffuse CO_2 degassing.

Geological setting

The Cape Verde archipelago (4,033 km^2) is located in the Atlantic Ocean, approximately 800 km west of Senegal, at latitudes between 14° 40′ and 17° 30′ N and longitudes between 21° 30′ and 25° 30′ W (Figure 1). The archipelago consists of ten islands and eight minor islets arranged in a westward opened horseshoe shape. The islands of Cape Verde are divided into the Northern or *Barlovento* (windward) islands (Santo Antão, São Vicente, Santa Luzia, São Nicolau, Sal, and Boa Vista) and Southern or *Sotavento* (leeward) islands (Maio, Santiago, Fogo, and Brava). The climate ranges from arid to semi-arid with two seasons: a moderate season (from November to June) and a ‘wet season’ (July to October) (Semedo and Brito 1995). The vegetation of the Cape Verde islands is sparse and consists of the drought-resistant species, mainly. The islands with most vegetation cover (Santo Antão, Fogo, and São Nicolau) also hold the largest vegetation cover in endemic biotopes. The archipelago is severely degraded, if not, places are already a desert: Sal, Boavista, and Maio (Lobin and Zizka 1987; Brochmann et al. 1997; Olehowski et al. 2008).

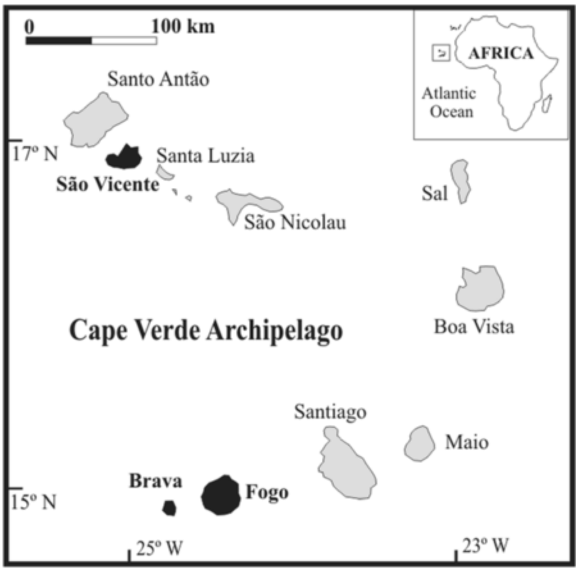

Figure 1 Geographic location of Cape Verde archipelago.

Cape Verde is consists of an intra-plate volcanic chain, *Cape Verde Rise*, the world’s highest intra-plate elevation in the ocean crust (Lodge and Helffrich 2006) and occupies a position on the passive margin of the African plate, coincident with important residual geoid and gravimetric and heat flow anomalies related to the well-characterized Cape Verde mantle plume (Courtney and White, 1986).The volcanic activity is originated by a hot spot located under a broad lithospheric swell that reflects the low velocity of the plate relative to the mantle plume (Holm et al. 2006). The onset of volcanism on the easternmost islands, which are deeply eroded and older, is in the middle Miocene (approximately 15 million years (Ma); Vinnik et al. 2012). Volcanic activity continued in Pliocene but on a reduced scale and migrated from east to west about approximately 6 Ma ago (Mitchell et al. 1983; Plesner et al. 2002; Duprat et al. 2007), which continues until today (Holm et al. 2008). During Holocene, volcanic activity occurred at Brava, Santo Antão, and Fogo islands (Foeken et al. 2009), but only Fogo Island has registered numerous historical eruptions since the first Portuguese colonization in the fifteenth century (Ribeiro 1960). The most recent eruptions occurred in 1951, 1995, and 2014 to 2015 (Ribeiro 1960; Torres et al. 1997; Heleno da Silva et al. 1999; Silva et al. 2015).

São Vicente island

São Vicente island (227 km^2) is one of the *Barlovento Islands*. Its outline resembles that of a rhombus with a major (E to W) diagonal of about 24 km and a minor (N to S) diagonal of about 16 km. According to Ancochea et al. (2010), São Vicente island arose in two main phases of construction: (i) the early phase, building up the lower São Vicente edifice (6.1 to 4.6 Ma) initiated as a shield volcano of greater dimensions than the present island, and (ii) the second phase started after the Praia Grande lateral collapse (4.5 Ma) and consisted of a refilling of the depression generated by landslide (4.5 to 1.3 Ma). This formation represents the upper São Vicente edifice. The recent volcanism (0.33 Ma; Jørgensen and Holm, 2002) is represented by a few well-preserved strombolian cones and some lava flows that were emitted to form land platforms gained from the sea at the east and northeast of island (Baia das Gatas, Calhau, Vulcão Viana, and Curral de João Paula) (Figure 2a).

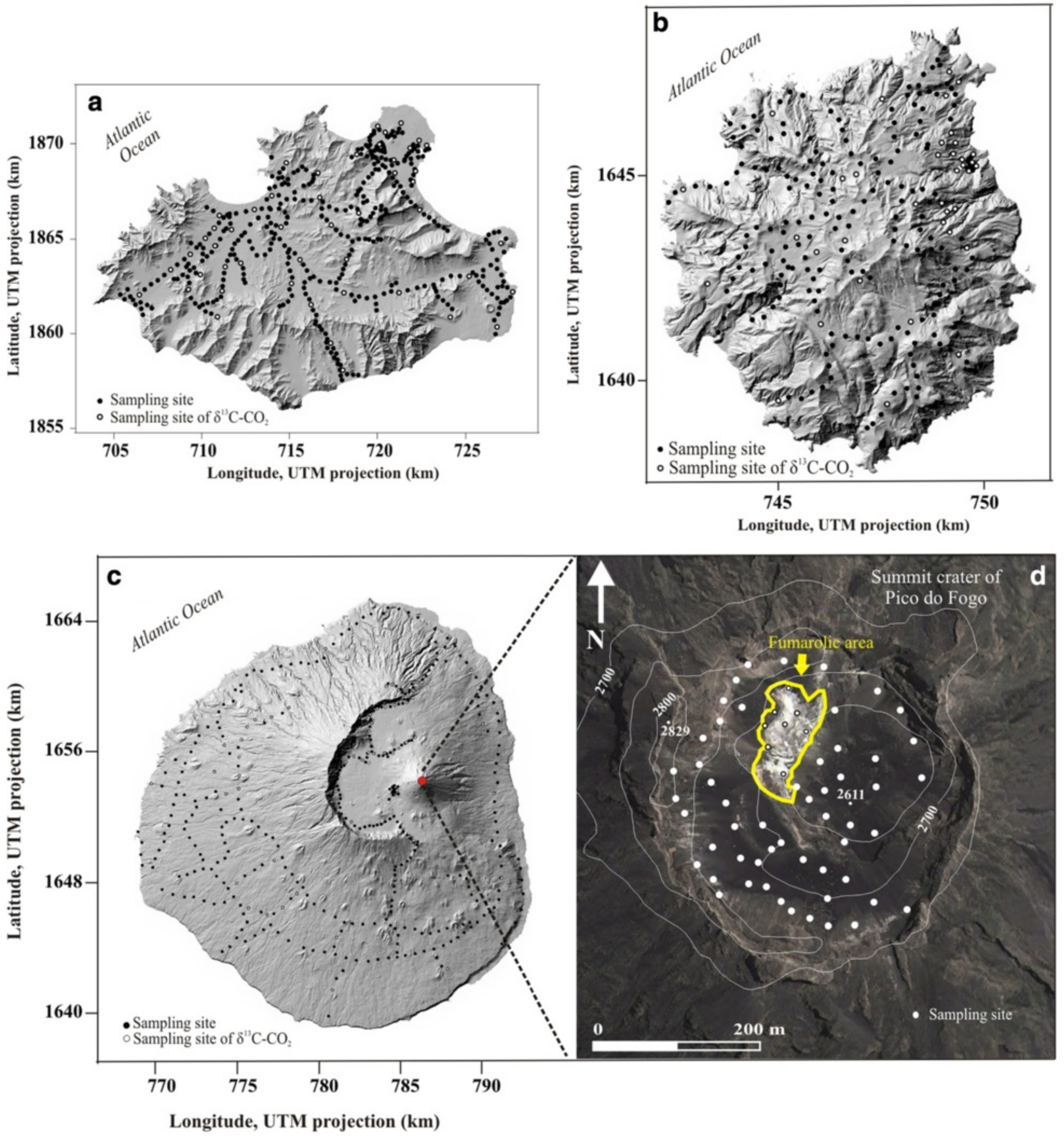

Figure 2 Sampling sites location. Location of sampling sites (black dots) of diffuse CO_2 efflux and sampling sites for $^{13}\delta C$ (CO_2) (open circles) at **(a)** São Vicente, **(b)** Brava, and **(c)** Fogo islands. Sampling sites of diffuse CO_2 efflux and $^{13}\delta$ C (CO_2) (white dots) correspond to **(d)** the summit crater of Pico do Fogo where yellow line indicates the extension of fumarolic area. Topographic map modified from Torres et al. 1998 with 50 m contour lines.

Brava island

Brava (67 km^2) is the westernmost island and it is located 18 km west of Fogo. The morphology of the island is characterized by a broadly circular shape and steep coastal slopes, cut by deep erosional valleys and extremely irregular plateau with a few major fluvial valleys and several closed (or formerly closed) depressions that correspond to modern phreatomagmatic craters and phonolite volcanic domes. Three volcano-stratigraphic units are identified: (i) Brava seamount stage or lower unit composed of alternating pillow lavas, hyaloclastites, and pillow breccia accumulations (approximately 3 to

2 Ma); (ii) alkaline-carbonatite complex (middle unit) produced by intrusions from shallow magma chambers (approximately 1.9 to 1.3 Ma) which have contributed to the sub-aerial development of the island; and (iii) a major erosive event and uplift pre-dating the younger volcanism (approximately 1.3 to 0.3 Ma) exposed the plutonic rocks (Madeira et al. 2010). During the last 300 ka, a sub-aerial, post-erosional volcanic phase covered the surface of the island with phonolite lava flows, domes, and pyroclasts which present a very fresh morphology, indicating a probable Holocene age (Madeira et al. 2010). Although no historical eruptions have occurred at Brava, the island is seismically active suggesting the occurrence of shallow intrusive activity. Recent seismic data (Faria and Fonseca, 2014) indicate that seismic activity is dominated by volcano-tectonic events with a local magnitude between 0.7 and 3.2, and most have epicenters offshore. Finally, it is important to point out that at Brava there are two areas (Baleia and Vinagre; Figure 2b) characterized by high -soil CO_2 contents which have produced several lethal accidents to animals as doves and goats (field observations).

Fogo Island

Fogo (476 km^2) is the fourth largest island in the archipelago of Cape Verde with a roughly circular shape (approximately 25 km of a diameter). The most prominent geological feature is Chã das Caldeiras, consisting of a 9-km north- to- south wide caldera opened towards the east and bounded on its northern, western, and southern sides by continuous and extremely steep cliff known as the Bordeira (approximately 20 km along). Pico do Fogo (2,829 m.a.l.s.) grew up inside of this caldera and is one of the world's most active volcanoes with about 30 eruptions since its discovery, the last occurring in 2014 (Figure 2c). The geological evolution of Fogo Island has been well reported by a few authors (Machado, 1965; Day et al. 1999). Day et al. (1999) and Foeken et al. (2009) proposed four phases for the geological evolution of Fogo: (i) uplift seamount series (approximately 4.5 Ma) composed of carbonatites and alkaline basalts; (ii) the Monte Barro group which includes the first sub-aerial lavas; (iii) the Monte Amarelo group which represents a period of intense volcanism which ended with the giant lateral summit collapse (approximately 123 to 62 ka; Foeken et al. 2009); and (iv) the post-collapse Chã das Caldeiras group (62 ka to present), where most of volcanic activity has occurred at the Chã das Caldeiras plain and a homogeneous distribution of numerous cinder cones outside the caldera along the three broadly radial volcanic rift zones (W, NNE, and SSE) of the island. Most of early historical eruptions (during the seventh and eighteen centuries) have occurred at the summit area of Pico do Fogo, whereas recent eruptions in Chã das Caldeiras have occurred mainly along WSW-ENE- oriented fissures (Day et al. 1999).

Pico do Fogo volcano is characterized by the existence of a fumarolic field situated NW inside the summit crater (Figure 2d) and composed by low- and high-temperature gas discharges (90°C to 100°C and above 200°C, respectively) with widespread sulfur precipitates at the surface, typical of hydrothermal alteration (Melián et al. 2008; Silva et al. 2011; Dionis et al. 2014). Faria and Fonseca (2014) reported that the most frequent seismic events at Fogo Islands are cigar-shaped, hybrid, long-period, volcano-tectonic events and spasmodic tremors. Volcano-tectonic events recorded on Fogo usually have a local magnitude ranging between 0.1 and 3.5, with epicenters located mostly inside Chã das Caldeiras and focal depths between 7 and 0 km (relative to the sea level), but most frequently near sea level.

Methods

In 2008, 2009, and 2010, three soil diffuse CO_2 emission surveys were carried out at São Vicente, Fogo, and Brava islands, respectively. To obtain a homogeneous distribution of sampling sites at each island, 400, 468, and 228 sites were selected for São Vicente, Fogo, and Brava islands, respectively (Figure 2), depending of the local geology, the main volcano-tectonic features and the accessibility. Within 468 sites selected for Fogo Island, 51 measurements were performed inside the summit crater of Pico do Fogo (0.142 km^2) (Figure 2d). All field works at Cape Verde archipelago were carried out during dry periods to minimize the influence of precipitation.

Soil CO_2 flux and chemical and isotopic composition

Measurements of soil CO_2 efflux were performed following the accumulation chamber method (Parkinson 1981) using two portable soil CO_2 flux instruments (West Systems, Italy). One of them was equipped with a non-dispersive infrared (NDIR) CO_2 analyzer LICOR-820, with a measurement range of 0 to 2,000 ppmV, an accuracy of concentration reading of 2% and a repeatability of ±5%. Due to the high-diffuse CO_2 emissions that are present in the summit crater of Pico do Fogo (Fogo Island) and Baleia and Vinagre areas (Brava Island), the soil CO_2 flux meter used at these areas was equipped with a Dräger Polytron IR CO_2 detector. It was composed by a double beam infrared CO_2 sensor compensated for temperature and atmospheric pressure. The accuracy on the flux measurement ranges between ±25% (for 0.5 to 5 mol m^{-2} d^{-1}) and ±10% (for 350 to 1,500 mol m^{-2} d^{-1}) and the detection limit is 1.5 g m^{-2} d^{-1}. Both analyzers were interfaced to a hand-held computer running data acquisition software.

With the aim to analyze the chemical and isotopic composition of soil gases, at each site samples were collected in 10-cc glass vials with a hypodermic syringe by inserting a 50 cm stainless probe at 40 cm depth in the ground following the method described by Hinkle and Kilburn (1979). Residual gas inside the probe was always purged before sampling. Content of CO_2 in the soil gas samples was analyzed by micro-chromatography with a VARIAN model 4900 (Agilent Technologies, USA) using a thermal conductivity detector and a 20-m PoraPLOT Q column using argon (Ar) as carrier gas. The temperature of the column and injector were 40°C and 60°C, respectively, and the injection time was 20 ms. The detection limit for CO_2 was estimated to be about 10 ppmV and the accuracy of the measurements about 2.5% on the basis of standard sample measurements. Soil temperature was also determined by inserting a thermocouple at each sampling site at a depth of 15 to 40 cm.

The $^{13}C/^{12}C$ ratios in CO_2 (expressed as $\delta^{13}C$-CO_2‰ vs. Vienna Pee Dee Belemnite (VPDB)) from soil gas samples were determined with a Thermo Finnigan MAT 253 isotopic ratio mass spectrometer (Thermo Fisher Scientific Inc., USA) with a continuous flow injection from a Finnigan Gas Bench II (Thermo Fisher Scientific Inc., USA) at the Geochemistry Laboratory of ITER-INVOLCAN (Canary Islands, Spain). The analytical error for $\delta^{13}C$ values is ±0.1‰. To investigate the carbon isotopic composition of the soil CO_2, a certain number of samples was selected for each survey (10%, 15%, and 29 % of total samples sites for São Vicente, Brava, and Fogo, respectively (Figure 2). Samples for $^3He/^4He$ analyses were collected from fumarolic discharges at summit crater of Pico do Fogo (Figure 2d) and from a groundwater cold-spring (Agua Vinagre, Figure 2b) in Brava Island and were analyzed at the Geochemical Research Center (University of Tokyo, Japan) following the methodology described by Sumino et al. (2001). $^3He/^4He$ data was corrected for air-derived contributions following the method described by Craig et al. 1978. About 50-cm^3 lead-glass bottles fitted with high-vacuum stopcocks at both ends were totally filled with gas (summit crater of Pico do Fogo) and water (Agua Vinagre). Dissolved helium and neon in the groundwater samples were extracted following the method described by Padrón et al. (2013). After extraction, helium isotopic ratios and helium and neon concentrations were measured following the method described by Sumino et al. 2001. The correction factor for helium isotope ratios was determined by measurement of an inter-laboratory helium standard named HESJ with recommended $^3He/^4He$ ratio of 20.63 ± 0.10 *Ra* (Matsuda et al. 2002).

Statistical and graphical treatment of the data

In order of distinguish the existence of different geochemical populations among acquired data, a statistical-graphical analysis (Sinclair 1974) was applied to the soil CO_2 efflux data from each survey. Probability plots are a useful practical tool in the analysis of soil geochemical data because of the common normal or log-normal character of such data. The normal or log-normal populations are usually interpreted as background and peak populations with different mean values. Soil gas contour maps were constructed using sequential Gaussian simulation (sGs), provided by the sgsim program (Deutsch and Journel, 1998; Cardellini et al. 2003), allowing us to estimate the total diffuse CO_2 output for each soil gas survey. The sGs procedure allows us to both interpolate the measured variable at not-sampled sites and assess the uncertainty of the total diffuse emission of carbon dioxide estimated for the entire studied area. The total emission rate of CO_2 was expressed as the mean value of 100 equiprobable sGs realizations, and it uncertainty was considered as one standard deviation of the 100 emission rates obtained after the sGs procedure. Spatial distribution maps of diffuse CO_2 emission were constructed using the average of the simulated values at each cell.

Results

Results are summarized in Table 1. At São Vicente Island, soil CO_2 efflux values ranged from detection limit (approximately 0.5 g m^{-2} d^{-1}) up to 10.1 g $m^{-2}d^{-1}$, with an average value of 1.3 g $m^{-2}d^{-1}$. The range of measured CO_2 efflux values is similar to the observed at other volcanic systems like Canary Islands (Hernández et al. 2012a). In order to distinguish the existence of different geochemical populations in the São Vicente CO_2 efflux data, a graphical statistical analysis was applied to the data showing two log-normal geochemical populations: background and peak (Figure 3a). Background population represented 68.2% of the total data with a mean of 0.5 g m^{-2} d^{-1} whereas peak population represented 1.7% with a mean of 7.6 g $m^{-2}d^{-1}$. An intermediate 'threshold' population which represents a mixing between background and peak values had a mean of 2.5 g $m^{-2}d^{-1}$ with 30.1% of the total soil CO_2 efflux data. The mean value of the background population (approximately 0.5 g m^{-2} d^{-1}) is smaller than the background values calculated for other volcanic system but it is similar that found in Timanfaya (approximately 0.4 g m^{-2} d^{-1}) by Hernández et al. (2012a) The existence of a peak population suggests a different source to the soil CO_2 degassing at São Vicente Island.

The experimental variogram for CO_2 efflux at São Vicente Island was fitted with a spherical model, nugget of 0.7, and range of 2,000 m. Following the variogram model, 100 simulations were performed over a grid of 23,132 (100 × 100 m) for an area of 227 km^2. The average CO_2 efflux map (Figure 4) shows that most of the island display background-like values, with the exception

Table 1 Statistical parameters in soil CO_2 flux data and estimated diffuse CO_2 emission rates

	Volcanic system		
	São Vicente (228 km^2)	**Brava (67 km^2)**	**Fogo (476 km^2)**
Volcanism	Pleistocene	Holocene	Historical
Survey date	August 2008	February 2010	May 2009
Number of sampling sites	400	228	468
Range soil CO_2 efflux (g m^{-2} d^{-1})	≤l.d to 10.1	≤l.d to 1,343	≤l.d to 15,685
Mean background population CO_2 efflux (g m^{-2} d^{-1})	0.5 (68.2%)	2.2 (98.9%)	1.0 (94.6%)
Mean peak population CO_2 efflux (g m^{-2} d^{-1})	7.9 (1.7%)	709.3 (0.6%)	1,704 (3.0%)
Mean intermediate population CO_2 efflux (g m^{-2} d^{-1})	2.5 (30.1%)	8.7 (0.5%)	85.2 (2.4%)
Peak/Background ratio CO_2 efflux	16	322	1,704
Total soil CO_2 emission (t d^{-1})	226 ± 14	50 ± 10	828 ± 5
Total soil CO_2 efflux (t km^{-2} d^{-1})	approx.0.9	approx. 0.7	approx. 1.7
Range soil δ^{13}C-CO_2 (‰ vs. VPDB)	−18.8 to −3.6	−20.8 to −1.3	−27.1 to −0.2
Range soil CO_2 conc. (ppmV)	354.8 to 1,985	935 to 521,300	743 to 405,933
Range temperature soil (°C)	23.8.0 to 39.5	19.1 to 43.4	18.8 to 293.8

Range of $\delta^{13}C(CO_2)$ and CO_2 concentration measured in soil gas samples and soil temperature at 40 cm is also showed.

of an area with relatively higher CO_2 efflux values (approximately 4.5 g m^{-2} d^{-1}). This area is recognized by several authors (Ancochea et al. 2010; Ramalho 2011) as the main Quaternary deposits of the island (dotted black line A). No significant values were observed along areas where recent volcanism has occurred (dashed black square B). The estimated average value for the total diffuse CO_2 released from São Vicente Island during this study was 226 ± 14 t d^{-1}. Given that the area of São Vicente Island is 227 km^2, we have estimated normalized value of approximately 0.9 t km^{-2} d^{-1}. This value is similar to the ones reported for other volcanic systems as Timanfaya volcano (Lanzarote, Canary Islands), with a normalized value in the range of 0.16 to 2.05 t km^{-2} d^{-1} (area of 252 km^2; Hernández et al. 2012a) and El Hierro, with a normalized values of approximately 0.7 t km^{-2} d^{-1} (area of 278 km^2; Melián et al. 2014).

At Brava Island, soil CO_2 efflux values ranged from detection limit (approximately 0.5 g m^{-2} d^{-1}) up to 1,343 g m^{-2}d^{-1}, with an average value of 19.2 g m^{-2}d^{-1}. The statistical-graphical analysis of soil CO_2 efflux data indicates the presence of two log-normal geochemical populations (Figure 3b): background and peak. Background population represented 98.9% of the total data with a mean of 2.2 g m^{-2}d^{-1} and a peak population represented 0.6% with a mean of 709.3 g m^{-2}d^{-1}. An intermediate 'threshold' population which represents a mixing between background and peak values had a mean of 8.7 g m^{-2}d^{-1} of CO_2 with 0.5% of the total soil CO_2 efflux data. Peak population may be considered as representative of CO_2 effluxes fed by an endogenous source as has been reported for other volcanic systems (Chiodini et al. 1998, 2001, 2008; Cardellini et al. 2003; Hernández et al. 2012a). A similar behavior is observed for São Vicente Island, with background values representing CO_2 efflux produced by biological activity in the soil although significantly higher than background values of São Vicente Island. The observed difference could be explained by development of

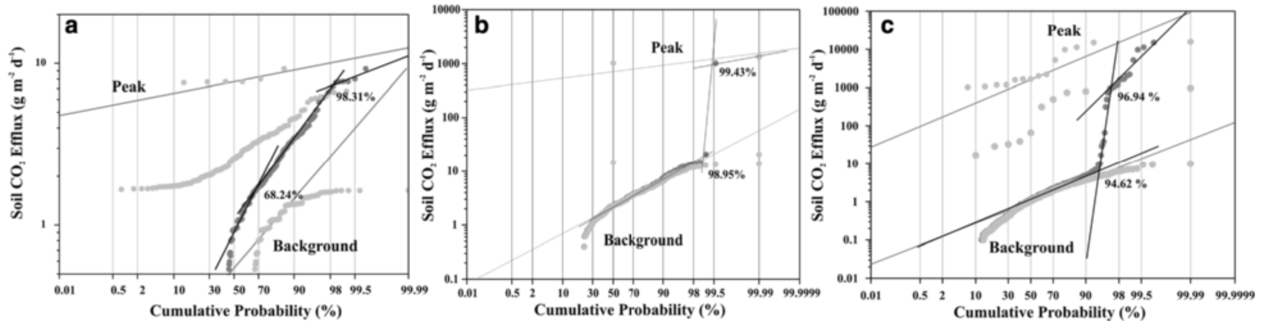

Figure 3 Cumulative probability plots of CO_2 efflux. (a) São Vicente Island; **(b)** Brava Island, and **(c)** Fogo Island. Solid black lines in the probability plots indicate different log-normal geochemical population in the original data. Solid gray lines indicate the separated background and peak log-normal populations.

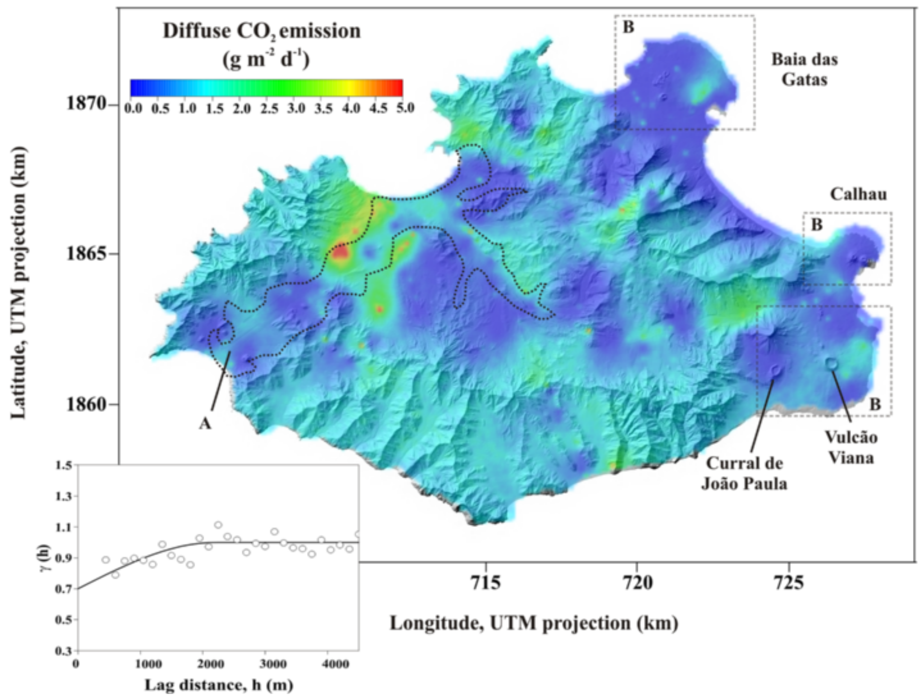

Figure 4 Spatial distribution map of diffuse CO_2 emission for São Vicente Island. The experimental and the modeled variogram used for the realization are showed at the bottom left. Dotted black line indicates Quaternary deposits A and dashed black square indicates B recent volcanic products with the main edifices: Curral de João Paula and Vulcão Viana. Modified volcano-stratigraphy defined by Ancochea et al. (2010).

vegetation since at São Vicente soils are less vegetated than in Brava. Even if the peak population for Brava Island represents a relatively low percentage of total data, its mean value (709.3 g $m^{-2}d^{-1}$) strongly supports the contribution of a deeper source (a volcanic-hydrothermal system).

The experimental variogram for CO_2 efflux at Brava Island was fitted with a spherical model, nugget of 0.65 and range of 1,450 m. Following the variogram model, 100 simulations were performed over a grid of 6,427 square cells (100 × 100 m) for an area of 67 km^2. Figure 5 shows the spatial distribution of soil CO_2 efflux where several areas were characterized by relatively high values located in the center of island. Madeira et al. 2010 have identified the main volcano-structural features (faults, calderas, and clusters of craters) in the center of island. One of major fault system proposed by Madeira et al. (2010), the Minhoto Fault Zone (MFZ), crosses the island in a NE-SW direction. From Figure 5, a diffuse degassing structure (Baleia DDS) can be observed, may be linked to MFZ and characterized by anomalous CO_2 efflux values, the highest measured throughout the island together with those measured at Vinagre DDS. No tectonic structure seems to be associated to Vinagre DDS. The estimated averaged value for the total diffuse CO_2 released from Brava Island during this study was 50 ± 10 t d^{-1}. If we normalize this value by the area of Brava (67 km^2), we obtain a value of approximately 0.7 t km^{-2} d^{-1}, similar to the one obtained for São Vicente Island.

At Fogo Island soil CO_2 efflux values ranged from approximately 0.5 (detection limit for LICOR) to 15,685 g $m^{-2}d^{-1}$, with an average value of 161.8 g $m^{-2}d^{-1}$. Maximum values were measured at the summit crater of Pico do Fogo, area of most intense surface geothermal activity in Cape Verde. As was done in the two previous cases, a statistical-graphical analysis was applied to the soil CO_2 efflux data to distinguish the existence of different geochemical populations. Two log-normal geochemical populations were identified: background and peak (Figure 3c). Background population represented 94.6% of the total data with a mean of 1.02 g m^{-2} d^{-1} and peak population represented 3.0% with a mean of 1,704 g $m^{-2}d^{-1}$. An intermediate 'threshold' population which represents a mixing between background and peak values had a mean of 85.2 g $m^{-2}d^{-1}$ of CO_2 with 2.4% of the total soil CO_2 efflux data. Peak population values were measured at the summit crater of Pico do Fogo, where intense fumarolic degassing occurs.

Distinct variogram model and sGs were applied to Fogo Island and Pico do Fogo crater areas. The experimental variogram for CO_2 efflux at Fogo Island was fitted with a spherical model, nugget of 0.4, and range of 5,500. Following the variogram model, 100 simulations were performed over a grid of 97,110 square cells (70 × 70 m) for an area of 476 km^2 for Fogo Island. In the case

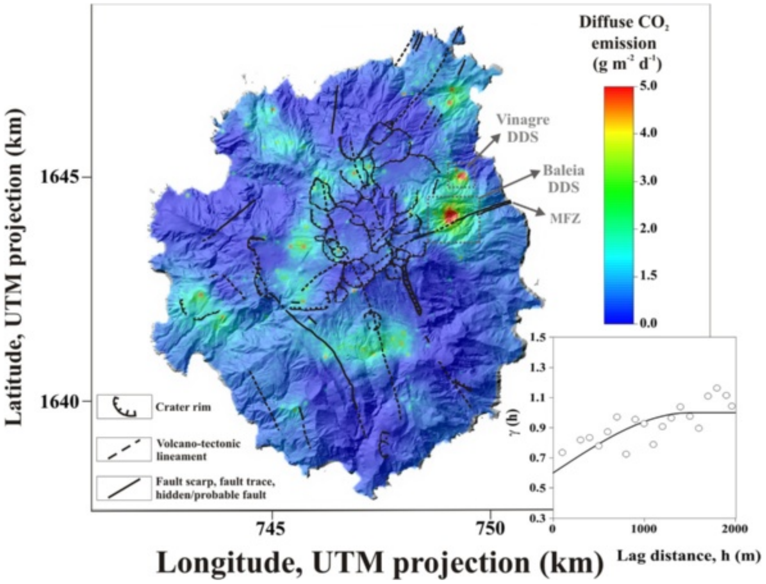

Figure 5 Spatial distribution map of diffuse CO_2 emission for Brava Island. The experimental and the modeled variogram used for the realization are showed at the bottom right, **w**ith modified volcano-tectonic structures defined by Madeira et al. (2010).

of Pico do Fogo crater, a spherical variogram model with nugget of 0.1 and range of 100 m was used to construct a grid of 15,745 square cells (3 × 3 m). Inspection of the average diffuse CO_2 emission map (Figure 6a) shows only background values outside the caldera, with relative maximum values approximately 4.5 g m^{-2} d^{-1}. Inside the caldera no significant soil CO_2 efflux values were observed, except those found inside the summit crater of Pico do Fogo (Figure 6b), possibly because most of the caldera is covered by recent lava flows. Inspection of Figure 6b shows that low soil CO_2 efflux values are located at the bottom of the crater, whereas higher CO_2 efflux values are observed close to the fumarolic area and other zones situated W and SE of the crater. It is remarkable that most of CO_2 efflux values are 3 or 4 orders of magnitude higher than the estimated background value for Fogo Island (1.02 g m^{-2} d^{-1}; in this work), supporting that anomalous CO_2 degassing is mainly fed by a magmatic source. Areas with the highest diffuse CO_2 efflux values were also characterized by a relatively high soil temperature (over 60°C) and by an intense surface hydrothermal alteration, which supports that degassing process is primary controlled by an advective mechanism generated by geothermal gradient (convection). The estimated average value for the total diffuse CO_2 released from Fogo Island during this study was 828 ± 5 t d^{-1}. In the case of the summit crater of Pico do Fogo (51 measuring sites), the estimated average value for the total diffuse CO_2 release was 147 ± 35 t d^{-1}. Given that the area of Fogo Island is 476 km^2, we have estimated an approximately 1.7 t km^{-2} d^{-1}, similar to obtained for São Vicente and Brava islands (this work) and other oceanic volcanic islands as Timanfaya volcano and El Hierro (values given above). However, normalized value for the summit crater of Pico do Fogo (1,035 t km^{-2} d^{-1}; 0.142 km^2) is similar to the normalized value found in other areas such as Solfatara crater (approximately 1,240 t km^{-2} d^{-1}; Chiodini et al. 2001) and higher than the computed in other studies carried out at volcanic craters such as Vesuvio (82.9 t km^{-2} d^{-1}; Frondini et al. 2004) and Vulcano (413.8 t km^{-2} d^{-1}; Chiodini et al., 1996; 537.3 t km^{-2} d^{-1}; Granieri et al. 2006) in Italy, Miyakejima (167 t km^{-2} d^{-1}; Hernández et al. 2001b) in Japan, and Teide (359.8 t km^{-2} d^{-1}; Pérez et al. 2013) in Canary Islands, Spain.

$\delta^{13}C$ (CO_2) isotopic composition

The $\delta^{13}C$ (CO_2) isotopic composition showed a wide range (Table 1) with an average value of −11.6‰, −11.3‰, and −17.2‰ vs. VPDB for São Vicente, Brava, and Fogo island, respectively. These mean values are heavier than the typical biogenic range for vegetated soils (−20‰; Craig 1953). A binary diagram of the $\delta^{13}C$ (CO_2) versus 1/[CO_2] for São Vicente, Brava, and Fogo data is explainable with two geochemical end-members: air, characterized by $\delta^{13}C$ (CO_2) = −8.0‰ vs. VPDB and [CO_2] = 400 ppm and biogenic CO_2 (Figure 7). To define the range of the biogenic end-member, we have considered that biogenic CO_2 in the soil is +4.4‰ heavier than the soil-respired CO_2 produced by roots, owing to the fractionation of diffusion within the soil (Cerling et al. 1991). Since the isotopic composition of soil organic matter is less than −20‰ (Craig, 1953), the isotopic composition for the biogenic soil CO_2 was defined as < −15.6‰ vs. VPDB. Figure 7 shows that most of the data plot in the shaded gray area

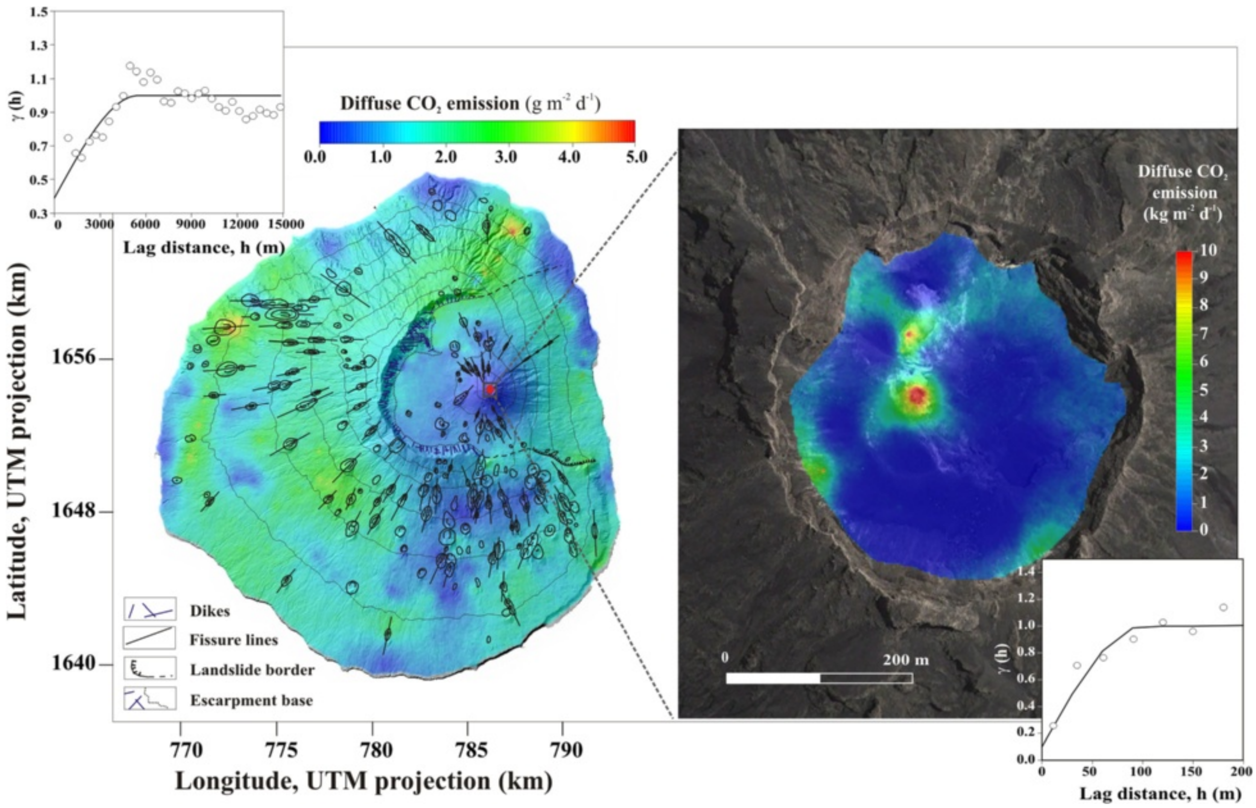

Figure 6 Spatial distribution map of diffuse CO_2 emission. For Fogo Island with modified volcano-structural map defined by Navarro 1999 (left) and for the summit crater of Pico do Fogo (right) (red dot in Figure 6 (left)). The experimental and the modeled variogram used for each realization are showed beside each map.

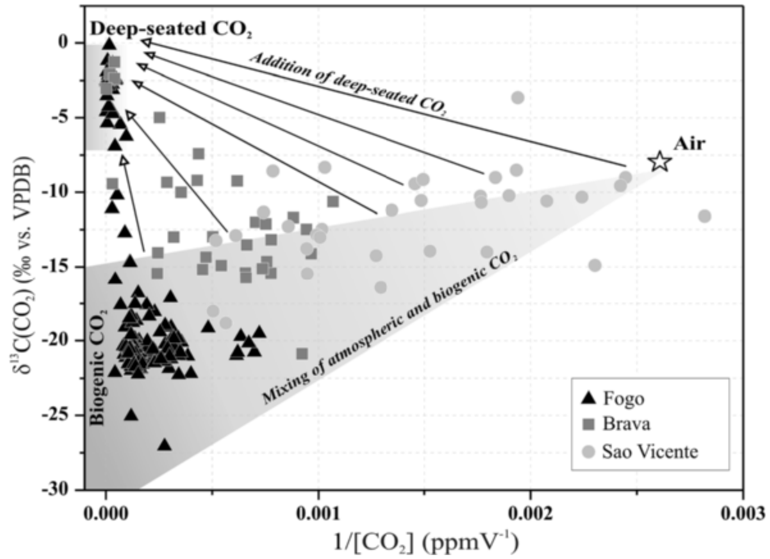

Figure 7 **Binary diagram of $^{13}\delta$ C (CO_2) versus $1/[CO_2]$ ($ppmV^{-1}$).**

which represents mixing of atmospheric and biogenic CO_2 for all studied islands. São Vicente values (light gray circles) plot close to the air end-member and deep-seated CO_2 enrichments are very small, almost negligible. Brava values (dark gray square) plot slightly above the biogenic CO_2 reservoir indicating a possible mixture between deep-seated CO_2 and a biogenic source that causes a graphical trend of samples along the arrows. The same behavior is observed for Fogo $\delta^{13}C$ (CO_2) values (black triangles), where most of the data plots close to the biogenic CO_2 reservoir with a small atmospheric contribution and a remarkable trend to the deep-seated CO_2. Samples with the strongest deep-seated CO_2 contribution were collected at the summit crater of Pico do Fogo where high values of diffuse CO_2 efflux were measured. The carbon isotope composition of the deep-seated CO_2 at summit crater of Pico do Fogo has been well constrained by the carbon isotopic data collected from the fumaroles by Dionis et al. (2014) (−4.48‰ to −4.25‰ with a mean of −4.25‰ (±0.14‰). Anomalous CO_2 efflux values (>1 kg m^{-2} d^{-1}) were also characterized by having heavier carbon isotope values, indicating an endogenous feeding source for the CO_2, i.e., degassing of a volcanic-hydrothermal system beneath Pico do Fogo volcano.

$^3He/^4He$ isotopic composition

The air-corrected $^3He/^4He$ ratios measured in the fumarolic discharges of Pico do Fogo summit crater (Fogo Island), varied from 7.73 to 8.53 Ra (where Ra is the atmospheric $^3He/^4He$ ratio = 1.393×10^{-6}; Sano et al. 2013a) in samples collected in 2009 (7.81 and 7.73 Ra; this study) and 2010 (8.53 Ra; Dionis et al. 2014). In the case of Brava, air-corrected $^3He/^4He$ ratios measured in Agua Vinagre groundwater spring in 2007 ranged between 4.86 and 6.51 Ra.

Discussion

Even when many studies have demonstrated that there is a significant relationship between diffuse CO_2 degassing and volcanic activity (see references herein), this relationship has been studied at the local scale for individual volcanoes. At the regional scale for selected areas like oceanic volcanic islands in a similar geological setting, a systematic study taking into account these facts has not yet been performed. To achieve find some parameter that links both concepts, we analyzed the relationship between diffuse CO_2 degassing and linked volcanic activity at Cape Verde volcanoes by applying different geochemical approaches; the results show *a priori* that magnitude of diffuse CO_2 degassing is significantly related. However, other factors may have a more important role on defining such a relationship. The first approach we used to investigate the relationship between both parameters was comparing the mean values of the background and peak populations obtained for each of the three studied volcanic systems. Results from the statistical-graphical analysis of soil CO_2 efflux data showed two overlapping log-normal geochemical populations (background (B) and peak (P)) for São Vicente, Brava, and Fogo islands (Figure 3). The estimated mean values of the background population were 0.5, 2.2, and 1.0 g m^{-2} d^{-1} for São Vicente, Brava, and Fogo, respectively, similar to the background values reported for others oceanic volcanic islands with similar soil, vegetation, and climate conditions, e.g., as the Canaries (Cumbre Vieja volcano: 1.8 g m^{-2} d^{-1}, Padrón et al. 2015; El Hierro Island: 1.4 g m^{-2} d^{-1}, Melián et al. 2014; and Timanfaya volcano: 0.4 g m^{-2} d^{-1}, Hernández et al. 2012a). On the other hand, mean values estimated for the peak populations were 7.6, 709, and 1,704 g m^{-2} d^{-1} for São Vicente, Brava, and Fogo, respectively. These peaks are from 1 to 3 orders of magnitude higher than the estimated background values, as has been also observed in other volcanic systems like Timanfaya volcano, Canary Islands (i.e., $B = 0.25$ g m^{-2} d^{-1} and $P = 5.9$ g m^{-2} d^{-1}, September 2010; Hernández et al. 2012a), Vesuvio summit cone, Italy ($B = 1.03$ g m^{-2} d^{-1} and $P = 29.5$ g m^{-2} d^{-1}; Cardellini et al. 2003); and Sierra Negra caldera in Galapagos ($B = 3.7$ g m^{-2} d^{-1} and $P = 22{,}000$ g m^{-2} d^{-1}; Padrón et al. 2012). The mean peak populations of Brava and Fogo islands indicate an important deep-seated contribution characterized by high CO_2 effluxes generated most likely by degassing processes of magmatic derived CO_2 as has been reported for other volcanic systems (Chiodini et al. 2001, 2008; Cardellini et al. 2003). However, direct comparison of mean background and peak values does not take into account other important factors such as the characteristics of soil and climate (different levels of development of soil horizons, organic matter content, vegetation, etc.), as well as the existence of diffuse degassing structures (Chiodini et al. 2001) which can greatly contribute to peak population values. These parameters can contribute directly to the background and peak populations at any volcanic area independently of the level of volcanic activity and geological age.

Another potential useful parameter that might link diffuse CO_2 degassing and volcanic activity is to compare the total diffuse CO_2 emissions between the different volcanoes under study. These values can be obtained from the spatial distribution maps of soil CO_2 efflux constructed by sGs, as described by Cardellini et al. (2003). The areas that contribute most to the total diffuse CO_2 degassing are those characterized by anomalous soil CO_2 efflux values (Figures 4, 5, and 6 for São Vicente, Brava, and Fogo islands, respectively). Inspection of the three maps shows that main the DDSs are located in Brava Island (Baleia DDS, possible be linked to

Minhoto Fault and Vinagre DDS a hidden fault or fracture) and summit crater of Pico do Fogo, which is the main diffuse CO_2 degassing area not only in Fogo Island but also in Cape Verde archipelago. To eliminate the effect caused by the size of the surveyed area, CO_2 emission needs to be normalized by the area (km^2) of study. The normalized values of diffuse CO_2 released from São Vicente, Brava, and Fogo Islands (approximately 0.9, approximately 0.7, and approximately 1.7 t km^{-2} d^{-1}, respectively) were found to be similar to other volcanic systems as Timanfaya volcano (Lanzarote), with a normalized value of 0.16 to 2.05 t km^{-2} d^{-1} (252 km^2; Hernández et al. 2012a) and El Hierro Island approximately 0.7 t km^{-2} d^{-1} (278 km^2; Melián et al. 2014), both located in the neighboring archipelago of Canary Islands. For proper intercomparison using normalized values, selected areas of study should have similar geological and volcanic characteristics (existence of DDS). In our study, the DDS showing the most intense diffuse CO_2 degassing was the summit crater of Pico do Fogo volcano. To compare its normalized value (1,035 t km^{-2} d^{-1} in 0.142 km^2) with other volcanic craters in Cape Verde with surface volcano-hydrothermal gas discharges at Brava and São Vicente Islands is not possible, since they do not exist.

A different approach could be to compare the contribution of different geochemical reservoirs to the CO_2 emissions. To do so, it is necessary to investigate the different origins of CO_2 in the diffuse emissions by analyzing the isotopic composition of the carbon in the soil CO_2. The addition of deep-seated CO_2 (which includes mantle-derived CO_2 and metamorphism of marine carbonate rocks) causes a graphical trend of samples along the arrows shown in Figure 7, towards $\delta^{13}C$ (CO_2) > −8‰ vs. VPDB (Javoy et al. 1978; Barnes et al. 1988) and $[CO_2] \sim 100\%$. São Vicente, Brava, and Fogo islands showed different degrees of atmospheric and biogenic CO_2 contributions. Only Brava and Fogo islands showed an endogenous CO_2 contribution with $\delta^{13}C$ (CO_2) values higher than those representative of a volcanic-hydrothermal source (Camarda et al. 2007). According to D'Alessandro and Parello (1997), $\delta^{13}C$ (CO_2) values between −1‰ and 1‰ may be subjected to isotopic fractionation due to diffusion processes and/or interaction with thermal aquifers. Since the carbon isotopic composition of the CO_2 discharged from fumaroles at the summit crater of Pico do Fogo is well constrained, this isotopic composition can be assumed as representative of deep-seated CO_2 (range from −4.5‰ to −4.1‰ with a mean of −4.2‰; ±0.1‰; Dionis et al. 2014). However, just comparing the behavior depicted by $\delta^{13}C$ (CO_2) vs. $1/[CO_2]$ diagram at the three areas of study, it does not seem to be a conclusive model to establish a relationship with the level of volcanic activity, because despite both Fogo and Brava volcanic systems have different geological ages and eruptive records (Fogo is the only island with historical eruptions) they show important addition of deep-seated CO_2 (Figure 7).

Finally, we considered to apply two geochemical tools such as the ratio of peak/background mean values, directly related to diffuse CO_2 degassing, and the magmatic helium emission as the $^3He/^4He$ isotopic ratios at São Vicente, Brava, and Fogo islands. $^3He/^4He$ isotopic in terrestrial fluids is the most powerful geochemical parameter to detect a mantle source (Sano et al. 1984; Sano

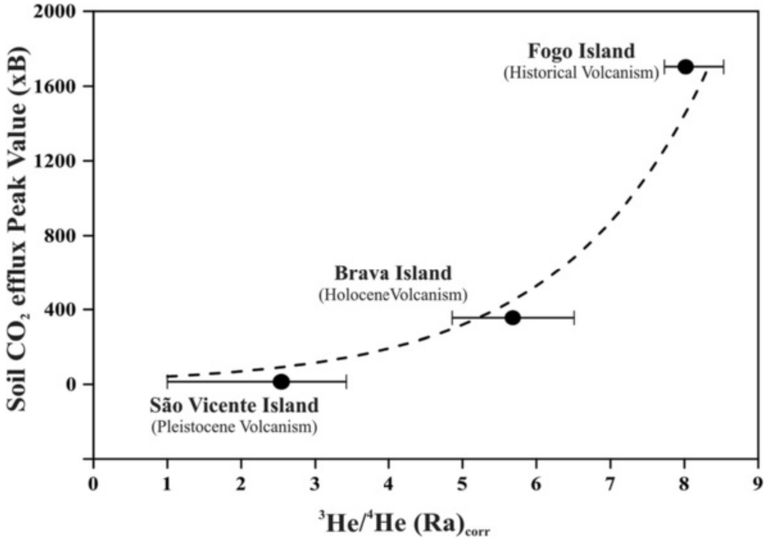

Figure 8 Relationship between soil CO_2 efflux peak values (×background) and the average $^3He/^4He$ ratio from Cape Verde archipelago. Horizontal bars represents the minimum and maximum $^3He/^4He$ ratio measured by Heilweil et al. (2009), in the case of San Antão and São Nicolau (assumed to be similar for São Vicente) and this work for Fogo and Brava islands.

and Fischer 2013b). Figure 8 shows the relation between the peak and background diffuse CO_2 efflux mean values ratio for each volcanic system and the helium-3 emission from Brava and Fogo Islands. Since samples for helium isotopic analysis, either gas emanations or groundwater, were not available at São Vicente to perform helium isotopic analysis, we have assumed for São Vicente the values measured at Santo Antão and São Nicolau islands by Heilweil et al. (2009) (0.9 to 3.4 Ra; ^{3}He/^{4}He). This assumption is supported by its geographical proximity and similar geological ages (Ancochea et al. 2010; Ramalho, 2011). The horizontal segment represents the minimum and maximum ^{3}He/^{4}He ratio measured by Heilweil et al. (2009), in the case of Santo Antão and São Nicolau (assumed to be similar for São Vicente) and this work for Fogo and Brava islands. The points represented the average of those values. Figure 8 shows a very good correlation between peak/background ratio and the helium-3 emission for São Vicente, Brava, and Fogo islands, as well as a good agreement with the geological ages of the three islands, directly related to the level of volcanic activity. Youngest sub-aerial volcanic rocks at São Vicente Island have a minimum age of 0.33 Ma (Pleistocene; Ancochea et al. 2010), whereas Brava Island likely has shown Holocene volcanism (Madeira et al. 2010). Unlike these two islands, Fogo is one of the most active volcanic islands in the world, with almost 30 historical eruptions since the beginning of European settlement around approximately 1,500 AD (Ribeiro 1960), the latest one taking place in 2014. The highest observed ^{3}He/^{4}He ratios were measured at the fumarolic discharges at the summit crater of Pico do Fogo are equivalent to the canonical ^{3}He/^{4}He isotopic ratio range accepted for MORB-derived fluids (8 ± 1 Ra; Craig and Lupton 1976; Kurz and Jenkins 1981; Lupton 1983), and these values are observed in others similar volcanic systems as Canary Islands (7.21 Ra (fumaroles discharge at Teide volcano); Pérez et al. 1996). This spatial distribution together with the observed differences between peak/background ratios seems to be in a very good agreement with the geological age of the islands and, therefore with the stage of the volcanic activity in Cape Verde. However, further studies at other volcanic oceanic islands will be required to better understand the importance using these geochemical tools.

Conclusions

This study present the first diffuse CO_2 degassing results in Cape Verde islands and its relationship with volcanic activity. The purely endogenous emission values (peak populations) measured in the three studied volcanic systems, São Vicente, Brava, and Fogo Islands, expressed as times the background values, seem to be directly related to the magmatic helium emission as ^{3}He/^{4}He isotopic ratios and therefore, to the present magmatic degassing and volcanic activity in Cape Verde. This statement is also supported by the relative geological ages of the eruptive activities occurred at the three islands. The summit crater of Pico do Fogo showed the maximum diffuse CO_2 efflux and the highest ^{3}He/^{4}He ratios of Cape Verde and is the only area showing fumarolic discharges in the archipelago. In addition, Fogo is the only Cape Verdean island with eruptive activity in historical times (<500 years). Although Brava island has shown an important recent seismic activity (Heleno da Silva et al. 2006) and obvious endogenous CO_2 emissions in specific areas (Baleia and Vinagre), it has not experienced historical eruptive activity and shows lower magmatic helium degassing values than Fogo. Finally, São Vicente, without Holocene eruptions, has shown the lower endogenous emission values.

Therefore, the above observations strongly indicate that diffuse CO_2 degassing is clearly linked to the level of volcanic activity and can be used as a useful geochemical tool for volcano monitoring programs in Cape Verde. To perform discrete CO_2 efflux surveys with a periodicity equivalent to the volcanic activity degree will provide important information about future episodes of volcanic unrest: higher at Fogo (mainly at the summit crater of Pico do Fogo), lesser at Brava and the lower at São Vicente islands.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

NMP and PAH conceived of the study, participated in its design and coordination, and helped to draft the manuscript. GM, FR, ZB, SMD, and EP participated in the design of the study and performed the statistical analysis. SMD wrote the first version of manuscript. GM, FR, GDP, JB, and PF collected data. HSu performed the ^{3}He/^{4}He analyses. SS, JMP, HSe, and JC are participating investigators. All authors read and approved the final manuscript.

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