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CO_2 fluxes of two lakes in volcanic caves in the Azores, Portugal

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ABSTRACT

This paper characterises diffuse CO_2 degassing from lakes located inside volcanic caves on the islands of Terceira and Graciosa (in the Azores archipelago, Portugal). The Algar do Carvão lake is located inside a volcanic pit on Terceira at an altitude of 92 m and has a surface area of 11,500 m^2 and a maximum depth of 8.2 m. The Furna do Enxofre lake is located inside a lava cave on Graciosa at an altitude of 500 m and has a surface area of approximately 300 m^2 and a maximum depth of 9.3 m.

The water temperature of both lakes is low, with values ranging between 11 °C and 13 °C, in both the winter and summer periods, and no variations are observed along their water columns. The electrical conductivity ranges from 585 μS cm^{-1} to 687 μS cm^{-1} in Furna do Enxofre and from 117 μS cm^{-1} to 131 μS cm^{-1} in Algar do Carvão, reflecting a higher mineralisation in the former lake. The pH values in Furna do Enxofre range between 6.50 and 6.58, which reflects the effect of CO_2 dissolution, while in Algar do Carvão, the pH values are more basic (7.42–8.53). The water types are Mg-HCO_3 for Furna do Enxofre and Na-HCO_3 for Algar do Carvão; the Mg-enrichment in Furna do Enxofre is associated with water–rock interactions, which are enhanced by the acidic environment.

Diffuse CO_2 flux measurements were made using the accumulation chamber method, with a total of 37 measurements split into two surveys at Algar do Carvão and 71 measurements during a single survey at Furna do Enxofre. The total CO_2 emitted from Furna do Enxofre was 6100 kg d^{-1}, which was much lower than that emitted from Algar do Carvão (0.32–2.0 kg d^{-1}). A volcanic origin was assigned to the lake on Graciosa due to the $\delta^{13}C$ isotopic signature of the CO_2; conversely, the CO_2 released in Algar do Carvão is derived from a biogenic CO_2 source.

Considering the surface areas of the studied lakes, the CO_2 flux is in the range of 1.5–6.7 t km^{-2} d^{-1} for Algar do Carvão and is 508.3 t km^{-2} d^{-1} for Furna do Enxofre.

1. Introduction

The compositions of volcanic lakes reflect the intersection between their magmatic-hydrothermal systems and the Earth surface (Christenson et al., 2015; Christenson and Tassi, 2015), and many lakes are sources of atmospheric CO_2 (Cole et al., 1994). This process is more evident in volcanic lakes because they are the centres of emission and condensation for volatile elements produced via magmatic activity.

On a global scale, CO_2 emission associated with subaerial and underwater volcanic activity is currently estimated to be close to 637 Mt yr^{-1}; 84.8% of which is from subaerial sources (~540 Mt yr^{-1}; Burton et al., 2013). According to Pérez et al. (2011), deep-seated volcanic lake CO_2 emissions correspond to approximately 94 ± 17 Mt yr^{-1}, approximately 17.4% of the subaerial volcanic CO_2 flux (Burton et al., 2013). This supports the relevance of quantifying the CO_2 flux emitted from volcanic lakes to estimate the global carbon budget.

In the last decade, several studies have been conducted to estimate the CO_2 emission from volcanic lakes spread all over the world (Kusakabe et al., 2008; Padrón et al., 2008; Mazot and Taran, 2009; Hernández et al., 2011; Mazot et al., 2011; Pérez et al., 2011; Caudron et al., 2012; Chiodini et al., 2012; Arpa et al., 2013; Mazot and Bernard, 2015; Sun et al., 2017). In the Azores Islands, several studies focusing on the CO_2 fluxes from major São Miguel lakes have also been performed, in particular for the Furnas (52–600 t d^{-1}; Andrade et al., 2016), Fogo (4.05 t d^{-1}; Andrade et al., 2018a), Santiago (0.22–5.56 t d^{-1}; Andrade et al., 2018b) and Congro (0.06–0.29 t d^{-1}; Andrade et al., 2018b) lakes. Melián et al. (2016) also proposed CO_2

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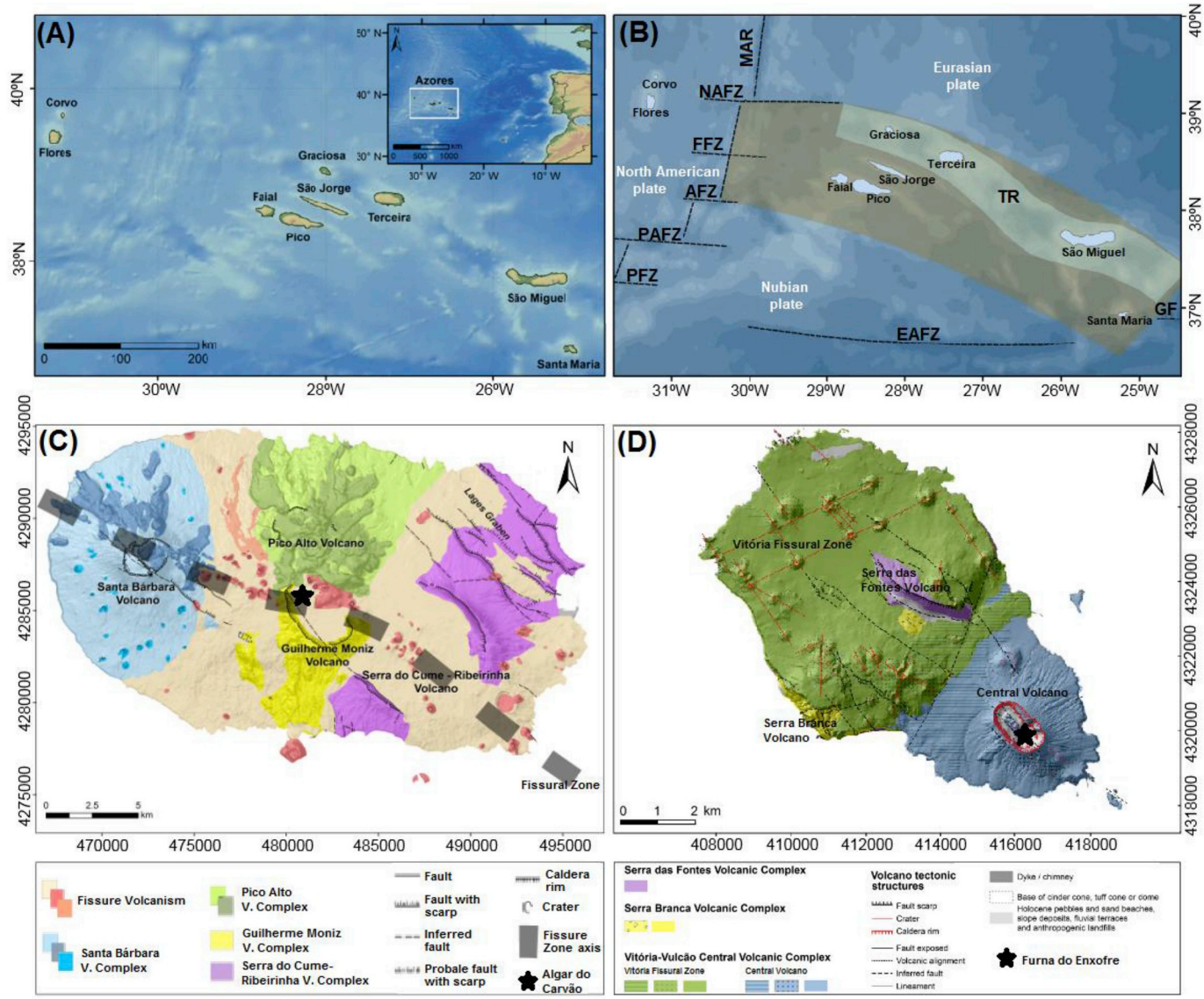

Fig. 1. Location of the studied area. (A) Setting of the Azores archipelago in the North Atlantic Ocean (modified from Marques et al., 2015); (B) location of the Azores and main morphotectonic features of the region (modified from Hipólito, 2009). The shaded area represents the sheared western segment of the Eurasia–Nubia plate boundary. Tectonic structures: MAR, Mid-Atlantic Ridge; TR, Terceira Rift; EAFZ, East Azores Fracture Zone; GF, Gloria Fault; NAFZ, North Azores Fracture Zone; FFZ, Faial Fracture Zone; AFZ, Açor Fracture Zone; PAFZ, Princesa Alice Fracture Zone and PFZ, Pico Fracture Zone. Azores bathymetry adapted from Lourenço et al. (1997); (C) framework of Terceira Island with the volcanic complexes and location of the studied lake (modified from Pimentel et al., 2016); (D) framework of Graciosa Island with the volcanic complexes and location of the studied lake (modified from Quartau et al., 2015).

flux estimates for the major lakes on the island of São Miguel, indicating a value of 0.61 t d^{-1} for the Sete Cidades Lake.

An extensive review of the literature was performed, and it appears that our study is the first that estimates the CO_2 fluxes of lakes located inside volcanic caves. The current study focuses in the so-called Furna do Enxofre (Graciosa) and Algar do Carvão (Terceira) lakes, both located in the Azores Islands. The main objectives of this study are to (1) characterise the water composition, (2) estimate the CO_2 flux in both lakes, (3) identify potential anomalous degassing areas, and (4) assess the CO_2 sources.

The Azores Islands consist of nine volcanic islands located in the North Atlantic Ocean and spread in a WNW–ESE alignment (Fig. 1A) along a complex geodynamic setting (Fig. 1B). Currently, there are 272 registered natural caves in the Azores dispersed through eight of the islands, the only exception being the island of Corvo. The caves are classified as lava caves (lava tubes), volcanic pits, cracks and erosion caves (Pereira et al., 2015). Perennial lakes only occur in Furna do Enxofre and Algar do Carvão.

2. Geological setting

2.1. The island of Terceira

The geology of Terceira is dominated by five main volcanic systems (Fig. 1C), namely, the four central volcanoes of Serra do Cume–Ribeirinha (> 401 kya; Hildenbrand et al., 2014), Guilherme Moniz (> 270 kya; Calvert et al., 2006), Pico Alto (> 141 kya; Gertisser et al., 2010) and Santa Bárbara (> 65 kya; Hildenbrand et al., 2014) and a fissure zone (> 43 kya; Calvert et al., 2006) (Zbyszewski et al., 1971; Madeira et al., 2015; Pimentel, 2015; Zanon and Pimentel, 2015) (Fig. 1C).

The tectonics of Terceira is dominated by NW–SE trending structures (Madeira, 2005; Madeira et al., 2015). Of the main NW–SE structures, the Lajes graben on the NE side of the island and the graben on the SE flank of the Santa Barbara volcano are the most relevant (Madeira, 2005).

A total of 69 caves have been mapped on Terceira (Pereira et al.,

Table 1
Characterisation of the studied lakes on the islands of Graciosa and Terceira.

Lake	Altitude (m)	Basin area (km^2)	Surf. Area (km^2)	Surf. work Area (km^2)	Max. Depth (m)	Volume (m^3)	Geol. Sett.
F. Enxofre	92	1.5×10^{-1}	1.2×10^{-2}	1.2×10^{-2}	9.3	$\sim 5.4 \times 10^4$	Lave Cave
Algar Carvão	500	1.9×10^{-1}	3.1×10^{-4}	3.0×10^{-4}	8.2	$\sim 1.5 \times 10^5$	Volcanic Pit

2015). The volcanic pit of Algar do Carvão was formed in two stages, the oldest part of the cave being associated with a 3200 year old trachyte lava flow. This flow has a chemical composition that corresponds to pantelleritic trachyte lava (Pimentel, 2015). The most recent flow corresponds to a conduit from a scoria cone that was active 2000 years ago (Nunes et al., 2004), known as the Algar do Carvão scoria cone. Zbyszewski et al. (1971) dated this eruption to 2115 ± 115 years ago. The Algar do Carvão scoria cone is associated with the fissure zone, which corresponds to an ~2-km-wide diffuse strip of WNW–ESE to NW–SE trending alignments of scoria and spatter cones (Pimentel, 2015; Pimentel et al., 2016).

The vent of the scoria cone corresponds to the cave ceiling and has a diameter of 17 m × 27 m and extends to a 45-m-vertical drop corresponding to the volcanic pipe conduit (Daza et al., 2014). The total horizontal extension of the cave is approximately 90 m, and the lake surface lies at a depth of approximately 80 m from the pit top.

The main features of Algar de Carvão are presented in Table 1. This water body has a surface area of 299 m^2, and the maximum depth measured during the current study was 8.2 m. The storage volume was estimated to equal 1.5×10^5 m^3. The water level is influenced by the seasonal variation of the precipitation that recharges the lake, accounting for the maximum depth of approximately 15–20 m reported by Carvalho et al. (2004).

2.2. The island of Graciosa

Graciosa has an elliptical shape that extends in the NW–SE direction (Madeira et al., 2015) and is approximately 13 km in length and 7 km in width, with a total surface area of 61.6 km^2. When compared to the other islands in the Azores, it is characterised by a smoother morphology, reaching a maximum elevation of 402 m on the southern rim of the caldera of its central volcano, which dominates the easternmost area of the island (Pacheco et al., 2013).

Three volcanic units define Graciosa (Fig. 1D) according to Gaspar and Queiroz (1995): the Serra das Fontes Volcanic Complex (620 ± 120 kya; Féraud et al., 1980), the Serra Branca Volcanic Complex (350 ± 40 kya; Féraud et al., 1980) and the Vitória–Central Volcano Volcanic Complex (12.2 ± 0.09 kya; Gaspar and Queiroz, 1995; Gaspar, 1996). Gaspar also takes into account, in the Vitória–Central Volcanic Complex, the contemporary units of the Vitória and Central volcanoes based on their geological setting and, subsequently, the type of volcanic activity present.

The tectonic structures on Graciosa show a prevailing NW–SE and NNW–SSE trend. A second set of structures present a NNE–SSW to NE–SW trend. Structures that are less common and, seemingly, with a smaller influence over the general structure of the island are those with an E–W trend (Gaspar, 1996; Hipólito, 2009; Hipólito et al., 2013; Madeira et al., 2015).

On Graciosa, a total of 11 caves have been mapped, with the Furna do Enxofre cave being the most famous (Pereira et al., 2015). Several authors have studied Furna do Enxofre and presented interpretative models regarding its genesis (Fouqué, 1873; Friedlander, 1930; Agostinho, 1935; Krejci-Graf, 1961; Saucier, 1965; Saucier and Roche, 1965; Ferreira, 1968; Maund, 1985; Gaspar, 1996).

According to Gaspar (1996), Furna do Enxofre is a basaltic lava cave located inside the caldera of the Central Volcano that resulted from a hydromagmatic explosion dated to approximately 12,000 years ago. A Hawaiian-type volcanic event inside the caldera must have occurred afterwards, producing 108 m^3 of magma and forming a lava lake. At some point, this lake drained through a volcanic conduit and formed the structure known today as Furna do Enxofre (Gaspar, 1996). A detailed study carried out on the magmatic processes on Graciosa shows that rock samples from Furna do Enxofre correspond to lavas of hawaiite composition (Larrea et al., 2014).

The opening of Furna do Enxofre is at an elevation of 137 m, and the cave is 194 m in length and 100 m in width at the entry point and 166 m in width near the lake area (Ogawa, 1989). The cave floor is characterised by a slope from the cave entrance to its lower area, where the lake is located.

Inside the cave, there is a fumarolic field consisting of one mud-pool-type fumarole, which has a typical hydrothermal composition with CO_2 as the main dry gas followed by other gases in lower concentrations, including H_2S, H_2, CH_4 and N_2 (Ferreira et al., 2005). CO_2, H_2S and ^{222}Rn are constantly released through the cave floors (Ferreira et al., 1993, 2005; Viveiros, 2003). In August 1992, two visitors died, and four others were injured due to high concentrations of CO_2 inside the structure. CO_2 values higher than 15 vol% were measured around that time close to the lake (Gaspar et al., 1998a).

The Furna do Enxofre lake exhibits a surface area of 11,950 m^2 and has an estimated storage volume equal to 5.4×10^4 m^3 (Table 1). Despite the maximum depth measured in the present study being equal to 9.3 m, the lake depth ranges from 9 m to 12 m, with higher values being reported after high precipitation seasons. Despite the seasonal variation, a decrease in the lake level of approximately 5.5 m was reported in the last quarter of the 20th century; this was associated with land-use changes on the caldera floor (Cruz et al., 2000).

3. Methodology

3.1. Water sampling

The lake water composition was characterised via the collection of samples along the water column, which was carried out in selected locations for each of the studied water bodies according to the maximum depth (P) (Fig. 2).

Sampling in Algar do Carvão was carried out in two surveys, the first in September 2016 (Algar_1) and the second in July 2017 (Algar_2). In Furna do Enxofre, only one survey was performed (March 2017; Enxofre_1) due to the hazardous CO_2 air concentrations that are present in the cave, especially during summer periods. In Algar do Carvão, samples were collected every 2 m during the second survey (maximum depth of ~8 m) and every 1 m during the first survey (maximum depth of ~4 m). Meanwhile, in Furna do Enxofre, samples were collected at 2-m-depth intervals (maximum depth of ~9 m). As a result, during the surveys a total of 16 samples were collected (Algar_1: 5 samples, Algar_2: 5 samples and Enxofre_1: 6 samples).

The physico-chemical parameters were registered immediately after sample collection (*i.e.,* pH, temperature and electrical conductivity), as well as the dissolved CO_2 concentrations and the alkalinity via titration following APHA-AWWA-WPCF (1985). For the first titration, an NaOH solution (1/44 M) was used as the titrant, and for the second the used titrant was an H_2SO_4 solution (0.05 M); both were added dropwise until the appropriate pH was reached, *i.e.,* pH values of 8.3 (dissolved CO_2) and 4.45 (alkalinity), respectively. All samples were filtered in the field

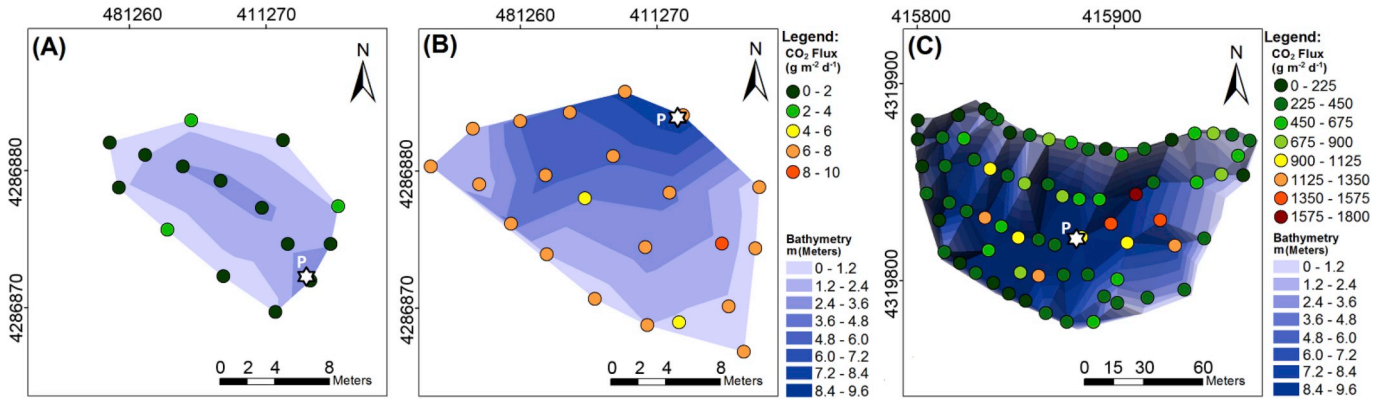

Fig. 2. Bathymetry and CO_2 flux measurement locations for the (A) first and (B) second surveys at Algar do Carvão and (C) for the Furna do Enxofre survey. The geochemical vertical profiles and isotopic sampling locations (P) for the Algar do Carvão and Furna do Enxofre lakes are also shown. The surveys were carried out in September 2016 (Algar_1), March 2017 (Enxofre_1) and July 2017 (Algar_2).

using 0.2-μm filters (cellulose acetate) and stored in polyethylene bottles. Samples for the cation analysis were also acidified with suprapur nitric acid immediately after sampling and filtering. The anions (Cl^-, SO_4^{2-}, NO_3^- and F^-) were determined via ion chromatography, the cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined via atomic absorption spectrometry, and silica was determined via spectrophotometry using the silicomolybdic method in the Hydrogeochemistry Laboratory of the Research Institute for Volcanology and Risk Assessment (IVAR, University of the Azores).

The results obtained using the different analytical methods were processed using the software programs PHREEQC Interactive (Parkhurst and Appelo, 1999) and AQUACHEM v.3.7 (Waterloo Hydrogeologic, 1998–1999).

Samples for the isotopic determinations were collected at the bottom of the water column, at the locations of the vertical profiles (Fig. 2). The sample collections for the $\delta^{18}O$ and $\delta^{2}H$ analyses were performed according a standard procedure (Clark and Fritz, 1997), and the water was stored in HDPE bottles. The $\delta^{18}O$ and $\delta^{2}H$ determinations were performed in the Stable Isotope Laboratory of Estación Biológica Doñana - CSIC (Spain), and a CRDS (Cavity Ring Down Spectroscopy) laser spectrometer Picarro L2130-i was used. The maximum error intervals were ± 0.3‰ for $\delta^{18}O$ and ± 3‰ for $\delta^{2}H$.

The sample collection for the dissolved inorganic carbon (DIC) $\delta^{13}C$ was performed using the sampling procedure proposed by the International Atomic Energy Agency (IAEA, 2017), and the analysis was carried out at the Stable Isotope Laboratory of Estación Biológica Doñana - CSIC (Spain) using a continuous flow isotope-ratio mass spectrometry system (Thermo Electron) consisting of a Flash HT Plus elemental analyser interfaced with a Delta V Advantage mass spectrometer. The maximum error interval was ± 0.15‰.

3.2. CO_2 flux measurements

CO_2 flux measurements were performed on the surfaces of the two lakes. Accordingly, 15 and 22 flux measurements were carried out at Algar do Carvão during the first and second surveys, respectively (Fig. 2A and B; Algar_1 and Algar_2, respectively), and a total of 71 measurements were performed at Furna do Enxofre (Fig. 2C) following a uniform pattern whenever possible. The measurement network covered areas of approximately 179 m^2, 299 m^2 and 11950 m^2 for the Algar_1, Algar_2 and Furna do Enxofre surveys, respectively. Some physico-chemical parameters of the water were registered in the same locations, *e.g.,* the temperature, electrical conductivity and pH. Depth measurements were also made using a Garmim ECHO™ 500c bathymetric probe.

The CO_2 measurements were performed using a modified accumulation chamber method (Chiodini et al., 1998); the details of this methodology, as well as its advantages and constrains, are described by Mazot and Bernard (2015). The portable device was equipped with an infrared LICOR LI-820 detector with a maximum scale of 20,000 ppm (accuracy ~3%), allowing measurements of the CO_2 flux in a range of 0–30,000 g m^{-2} d^{-1} (West Systems, 2014). The reproducibility of the method was estimated to be 10% for CO_2 fluxes up to 10,000 g m^{-2} d^{-1} by Chiodini et al. (1998).

The calibration of the CO_2 flux instrument was made in the Laboratory of Gas Geochemistry at IVAR (University of the Azores), according a three-step sequential procedure, allowing corrections of the data acquired along the field surveys using the slope of the calibration curve as a correction factor.

3.3. Statistical approach applied to the CO_2 flux data

Data regarding diffuse CO_2 measurements were processed using the graphical statistical approach (GSA) (*e.g.,* Chiodini et al., 1998). GSA is based on cumulative probability plots, which help to identify the presence of different populations in geochemical data (Sinclair, 1974), which may in turn correspond to different processes and, in the particular case of CO_2, to different sources (biogenic and volcanic-hydrothermal (*e.g.,* Chiodini et al., 1998; Cardellini et al., 2003; Andrade, 2014; Viveiros et al., 2010; Andrade et al., 2016; Viveiros et al., 2017). Statistical descriptors (the mean and standard deviation), as well as the proportion of each partitioned lognormal population, were graphically estimated via probability plots according to the methodology proposed by Sinclair (1974). The mean and the 95% confidence interval of the mean were computed using the Sichel *t* estimator (David, 1977). This methodology has been applied to many studies related to CO_2 spatial analyses in several volcanic regions (*e.g.,* Chiodini et al., 1998; Cardellini et al., 2003; Viveiros et al., 2010; Andrade et al., 2016; Sun et al., 2017; Viveiros et al., 2017).

The sequential Gaussian simulation (sGs) interpolation method (Deutsch and Journel, 1998; Cardellini et al., 2003) has been used in several spatial CO_2 flux studies to produce degassing maps; however, because (1) the original data did not follow a normal distribution, (2) each survey had less than 100 measurements, and (3) consequently, the normal scores could not be calculated, the use of sGs (Cardellini et al., 2003) was excluded from this study. In addition, the experimental variograms did not show spatial structures conducive to the possibility of using Kriging as an interpolation method. Therefore, the deterministic method of inverse distance weighting (IDW) was used to interpolate the data and generate CO_2 flux distribution maps (Landim, 2003) considering four neighbouring points for the Algar do Carvão lake surveys and six neighbouring points for the Furna do Enxofre survey. The ArcGis 10 software (ESRI) was used for these interpolations.

Table 2
Descriptive statistics for the water composition in the Furna do Enxofre and Algar do Carvão lakes: the water chemistry data collected in profiles along the water column including the primary variables (temperature, pH and electrical conductivity), the major-ion composition and the SiO_2 content and the values for electrical conductivity from PHREEQC. The sampling surveys took place in September 2016 (Algar_1), March 2017 (Enxofre_1) and July 2017 (Algar_2).

Location	Depth (m)	T	pH	Cond.	CO_2	HCO_3	Cl	SO_4	NO_3	Na	Mg	K	Ca	SIO_2
		°C		µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Enxofre	**0**	13.70	6.58	585.00	58.10	262.91	96.12	55.11	7.11	40.89	39.63	4.65	35.43	57.16
	2	13.80	6.50	648.00	64.40	231.80	98.24	55.30	7.15	39.37	54.76	5.50	46.68	58.02
	4	13.70	6.58	687.00	59.20	223.87	91.85	54.19	6.76	41.61	65.49	7.41	37.67	57.69
	6	13.70	6.59	638.00	57.50	240.95	96.77	55.55	6.75	41.59	52.49	4.31	36.93	56.73
	8	13.70	6.58	625.00	55.50	237.90	94.60	55.21	6.43	39.81	45.54	4.87	29.14	57.48
	9	13.70	6.53	612.00	59.60	234.85	93.30	54.84	6.23	40.80	48.57	3.67	29.71	56.37
	Max.	13.80	6.59	687.00	64.40	262.91	98.24	55.55	7.15	41.61	65.49	7.41	65.49	46.68
	Min.	13.70	6.50	585.00	55.50	223.87	91.85	54.19	6.23	39.37	39.63	3.67	39.63	29.14
	Mean	13.72	6.56	632.50	59.05	238.71	95.15	55.03	6.74	40.68	51.08	5.07	51.08	35.93
	Sta. Dev.	0.04	0.04	34.56	3.00	13.22	2.35	0.47	0.36	0.92	8.85	1.30	8.85	6.40
	Med.	13.70	6.58	631.50	58.65	236.38	95.36	55.16	6.76	40.85	50.53	4.76	36.18	57.32
Algar_1	**0**	11.90	7.42	129.00	4.10	51.24	21.15	5.25	0.78	33.63	0.02	2.66	2.04	52.67
	1	11.90	7.44	127.00	4.70	53.07	22.33	5.32	0.53	31.74	0.02	2.63	1.35	56.05
	2	11.80	7.53	126.00	5.00	54.90	20.40	5.06	0.64	32.01	0.10	2.66	1.30	55.17
	3	11.90	7.56	128.00	4.60	56.12	20.54	5.15	0.72	32.17	0.11	2.56	1.72	55.70
	4	11.90	7.62	131.00	5.00	57.34	22.86	4.85	0.55	31.75	0.19	2.58	2.00	59.41
	Max.	11.90	7.62	131.00	5.00	57.34	22.86	5.32	0.78	33.63	0.19	2.66	2.04	59.41
	Min.	11.80	7.42	126.00	4.10	51.24	20.40	4.85	0.53	31.74	0.02	2.56	1.30	52.67
	Mean	11.88	7.51	128.20	4.68	54.53	21.46	5.13	0.64	32.26	0.09	2.62	1.68	55.80
	Sta. Dev.	0.04	0.08	1.92	0.37	2.42	1.09	0.18	0.11	0.79	0.07	0.05	0.35	2.41
	Med.	11.90	7.53	128.00	4.70	54.90	21.15	5.15	0.64	32.01	0.10	2.63	1.72	55.70
Algar_2	**0**	12.50	7.95	117.00	19.00	43.92	21.51	4.57	0.55	28.34	0.12	2.30	1.46	54.67
	2	12.60	7.97	118.00	15.60	44.53	21.48	4.48	0.42	28.95	0.14	2.35	1.49	53.12
	4	12.60	8.38	119.00	26.70	43.31	20.84	4.51	0.58	29.71	0.15	2.39	1.45	51.73
	6	12.80	8.40	119.00	25.90	45.14	20.64	4.45	0.74	29.04	0.13	2.31	1.38	51.07
	8	12.60	8.53	126.00	27.00	61.00	20.39	4.56	0.98	28.60	0.11	2.29	1.31	49.92
	Max.	12.80	8.53	126.00	27.00	61.00	21.51	4.57	0.98	29.71	0.15	2.39	1.49	54.67
	Min.	12.50	7.95	117.00	15.60	43.31	20.39	4.45	0.42	28.34	0.11	2.29	1.31	49.92
	Mean	12.62	8.25	119.80	22.84	47.58	20.97	4.51	0.65	28.93	0.13	2.33	1.42	52.10
	Sta. Dev.	0.11	0.27	3.56	5.21	7.53	0.50	0.05	0.21	0.52	0.02	0.04	0.07	1.84
	Med.	12.60	8.38	119.00	25.90	44.53	20.84	4.51	0.58	28.95	0.13	2.31	1.45	51.73

4. Results and discussion

4.1. Water composition

The water compositions of both the Furna do Enxofre and Algar do Carvão lakes are shown in Table 2. At Algar do Carvão, the water level variation shows a seasonal effect: along the Algar_1 survey, made at the end of the summer period, the measured lake level is lower due to the reduced inflow compared to measurements made along the Algar_2 survey.

Despite an estimated drop of approximately 5.5 m in the water level at Furna do Enxofre that occurred approximately 30–40 years ago due to land-use changes on the bottom of the caldera (Cruz et al., 2000), the water level depicts small seasonal variations, on the order of 10–30 cm (Gaspar et al., 1993a, b).

The lake waters are cold, with small temperature variations between 13.7 °C and 13.8 °C (Furna do Enxofre) and between 11.8 °C and 11.9 °C and between 12.5 °C and 12.8 °C for Algar_1 and Algar_2, respectively. The temperature profile indicates that the values are relatively constant with depth in both lakes (Fig. 3A); this holomictic character, with continuous mixing along the water column throughout the year, is explained by the setting of the lakes inside caves, in contrast to the monomictic character of the deeper lakes in the Azores Islands (Cruz and Andrade, 2015; Andrade et al., 2016). The surface temperature values present a narrow range, on the order of 13.7–14.0 °C at Furna do Enxofre and 11.5–12.5 °C at Algar do Carvão.

The pH measurements depict a sharp difference between the two lakes, with values ranging between 6.50 and 6.58 in Furna do Enxofre and between 7.42 and 7.62 (Algar_1) and between 7.95 and 8.53 (Algar_2) in Algar do Carvão (Fig. 3B). The latter range, which also shows a slight increase at the bottom of the Algar do Carvão lake along the Algar_2 survey compared to that along the Algar_1 survey, is likely due to the replenishment of the lake itself. During Algar_2, the volume of water storage was much higher, as shown by the greater depth, therefore suggesting recharge via meteoric water; during percolation through the soil, such water is expected to become enriched in CO_2 (Drever, 1997). As percolation is expected to be fast due to the geologic environment, the CO_2 content is not completely consumed by water–-rock interactions; however, a greater extent of silicate dissolution processes may explain a higher pH value.

At the surface, the pH values are very homogeneous in Furna do Enxofre (6.30–6.60). Meanwhile, during Algar_2, the range of measured values was slightly larger (7.40–8.40) than that seen during Algar_1 (7.40–7.50).

The electric conductivity (EC) values were as high as 687 µS cm^{-1} in Furna do Enxofre and much lower in Algar do Carvão (126–131 µS cm^{-1} during Algar_1 and 117–126 µS cm^{-1} during Algar_2); these values were rather constant along the water column (Fig. 3C). The Furna do Enxofre EC measurements represent the highest recorded values for lakes in the Azores (Cruz et al., 2006) and are much higher than the mean value measured in groundwater springs discharging from perched-water bodies in the Azores (188.9 µS cm^{-1}; Cruz and Amaral, 2004). The EC indirectly reflects the magnitude of the overall dissolved content in the water; therefore, the sharp difference between the values measured in the two lakes depicts the higher contribution of water–rock interactions at Furna do Enxofre. Silicate–water reactions due to the incongruent dissolution of silicate minerals release silica and cations into the water and lead to an increase in the pH and in

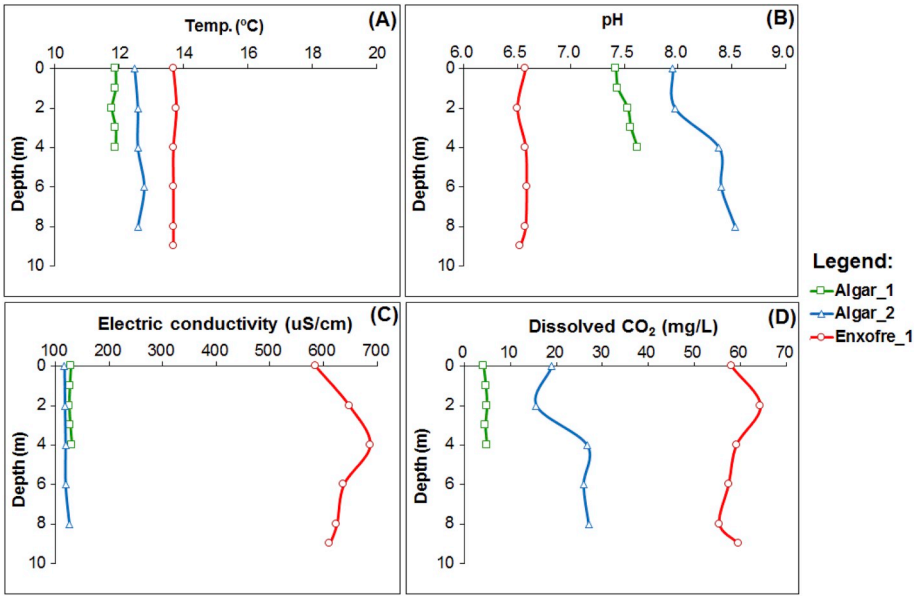

Fig. 3. Geochemical profiles for several physico-chemical parameters: (A) temperature; (B) pH; (C) electrical conductivity and (D) dissolved CO_2. The sampling surveys took place in September 2016 (Algar_1), March 2017 (Enxofre_1) and July 2017 (Algar_2).

the HCO_3 content (Appelo and Postma, 1993), therefore neutralising the fluid acidity.

The dissolved CO_2 is in the range of 55.5–59.6 mg L^{-1}, which is significantly higher than the values measured in Algar do Carvão (4.1–5 mg L^{-1} for Algar_1 and 19–27 mg L^{-1} for Algar_2); the bicarbonate content is also much higher in Furna do Enxofre (234.85–262.91 mg L^{-1}) compared to Algar do Carvão (51.24–57.34 mg L^{-1} and 43.31–61 mg L^{-1} for the Algar_1 and Algar_2 surveys, respectively, Fig. 3D), as well as other lakes in the Azores (Cruz et al., 2006). The calculated pCO_2 ranges were between $10^{-1.14}$ and $10^{-1.23}$ for Furna do Enxofre and between $10^{-2.69}$ and $10^{-3.73}$ for Algar do Carvão, with the latter values being similar to the atmospheric partial pressure ($10^{-3.50}$; Drever, 1997).

The major-ion composition was similar to data reported by Cruz et al. (2006) and Antunes (2008), and a Piper-type diagram shows that the water types are Mg-HCO_3 in Furna do Enxofre and Na-HCO_3 in Algar do Carvão (Fig. 4). The Mg-enrichment trend observed for Furna do Enxofre is not common in lakes located in the Azores Islands because these water bodies usually present a dominant Na-HCO_3 type with a diverse degree of Cl contributions indicating a marine source (Cruz et al., 2006; Antunes, 2008).

The Mg-enriched waters from Furna do Enxofre likely reflect the contribution from water–rock processes, which also explains the much higher overall dissolved solids content in this lake compared to others in the Azores (mean EC = 96.2 μS cm^{-1}; Cruz et al., 2006) and is similar to the enrichment in alkali-earth metals observed in groundwater from basaltic-dominated perched-water aquifers (Cruz and Amaral, 2004). Table 2 indicates that the Na/Mg molal ratio in Furna do Enxofre is equal to 0.84, which is lower than the values of the springs discharging from the perched-water aquifers in the Azores (6.68 according to Cruz and Amaral (2004)). These differences highlight the Mg-enrichment at Furna do Enxofre; in addition, the waters from this lake are immature, as indicated by samples, which lie in the $Mg^{1/2}$ corner on the Na/1000–K/100–$Mg^{1/2}$ ternary plot proposed by Giggenbach (1988; Fig. S1), revealing that these waters are preferentially solubilising Mg from the host basaltic rocks. Meanwhile, the Algar do Carvão samples depict a higher Na + K relative content despite also being immature. This is also consistent with the Na/K molal ratio, which is equal to 13.61 in Furna do Enxofre and 20.00 in Algar_1 and higher than the values for the groundwater in the perched aquifers (9.77; Cruz and Amaral, 2004), suggesting low-temperature water–rock interaction processes in both lakes because K portioning between aluminosilicates and water is temperature dependent (Ellis and Mahon, 1977). This latter effect is shown by the lower Na/K molal ratio computed for the thermal waters in the Azores (Freire et al., 2014).

The silicate mineral dissolution process is enhanced in acidic environments (Drever, 1997), as in that at Furna do Enxofre, which occurs due to the dissolution of volcanic gases. The higher level of HCO_3 enrichment in Furna do Enxofre, about five times higher than that in Algar do Carvão (Fig. 5E), can also be explained by the dissolution of silicate minerals.

The variation in the major ions and SiO_2 along the water column is shown in Fig. 5, depicting a higher content in Furna do Enxofre, as well a constant pattern with depth for the anions. At Furna do Enxofre, an increase in Ca, Mg and K is observed at the 4–6-m-depth level (Fig. 5B–D), and this enrichment includes, in addition to the water–rock interactions, seepage of groundwater that mixes with the lake water at that depth. This input may also be increasing the dissolved CO_2 and slightly lowering the pH at this depth level but should be only a minor driver of the water composition, as pointed out by Cruz et al. (2006) when considering the As content.

The SiO_2 content ranges between 56.37 mg L^{-1} and 58.02 mg L^{-1} for the Furna do Enxofre survey and between 52.67 mg L^{-1} and 59.14 mg L^{-1} and between 49.92 mg L^{-1} and 54.67 mg L^{-1}, for the Algar_1 and Algar_2 surveys, respectively. The high SiO_2 content in these lakes, when compared to that observed in the groundwater discharging from perched-water bodies in the Azores (mean = 38.17 mg L^{-1}; Cruz and Amaral, 2004), might be explained by the dissolution of silicate minerals and even obsidian, as suggested by Carvalho et al. (2004), and suggests that the lake waters are oversaturated relative to some silica solid phases. The computation of the saturation indexes using PHREEQC (Parkhurst and Appelo, 1999) shows that, in both lakes, the water is oversaturated with respect to quartz (SI in the range of $10^{0.8}$–$10^{0.81}$ in Furna do Enxofre and in the range of $10^{0.75}$–$10^{0.85}$ in Algar do Carvão) and chalcedony (SI in the ranges of $10^{0.33}$–$10^{0.34}$ and $10^{0.28}$–$10^{0.37}$, respectively). The high silica content also explains the occurrence of siliceous speleothems inside Algar do Carvão, resulting from precipitation from groundwater discharged from fractures and enriched in SiO_2 due to water–rock interactions (Daza, 2015). In the case of Furna do Enxofre, the contribution of groundwater seepage to the high SiO_2 content is also not excluded as mentioned above.

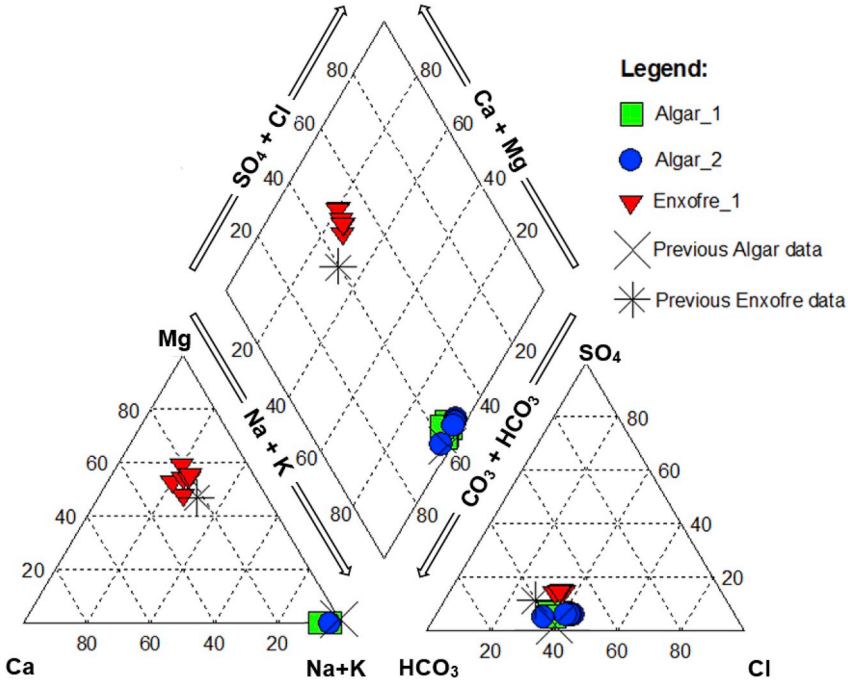

Fig. 4. Major-ion relative composition represented via a Piper-type diagram (previous data from Antunes, 2008).

The isotopic content for $\delta^{18}O$ is equal to −4.95‰ and −4.39‰ and for $\delta^{2}H$ is equal to −18.35‰ and −18.10‰ for Furna do Enxofre and Algar do Carvão, respectively, with these contents being close to the local meteoric water line (Fig. 6). These results confirm that, in both lakes, the water has a meteoric origin, as suggested by Cruz et al. (2000). Values for both lakes plot close to the isotopic signature of the groundwater sampled from wells drilled in Graciosa and Terceira, which means that they are not affected by seawater intrusion or by

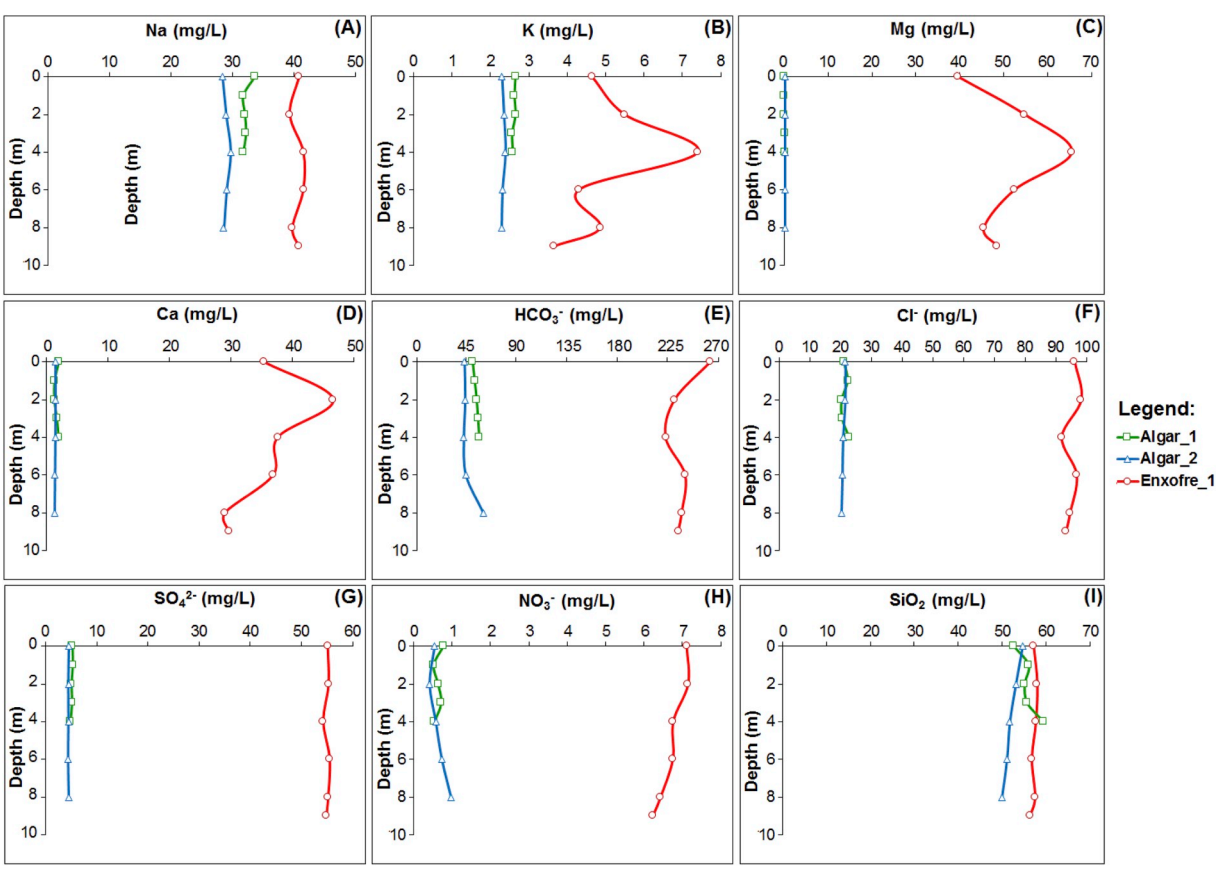

Fig. 5. Geochemical profiles for the major-ion composition: (A) Na; (B) K; (C) Mg; (D) Ca; (E) HCO_3; (F) Cl; (G) SO_4; (H) NO_3) and (I) SiO_2. The sampling surveys took place in September 2016 (Algar_1), March 2017 (Enxofre_1) and July 2017 (Algar_2).

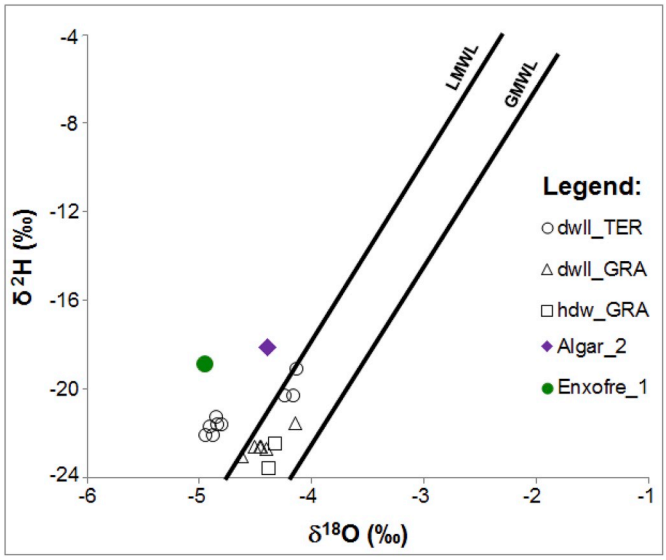

Fig. 6. Relationship between $\delta^{18}O$ (‰) and $\delta^{2}H$ (‰). The global meteoric water line from Craig (1961) and the local meteoric water line ($\delta^{2}H = 8\ \delta^{18}O + 15$) from Rodrigues (1995) are included, as well as the groundwater data from Cruz and Andrade (2017). Drilled wells: dwll; hand-dug-wells: hdw.

isotopic enrichment resulting from evaporative effects (Cruz and Andrade, 2017).

4.2. CO_2 fluxes

The carbon dioxide flux values measured at the Furna do Enxofre lake surface range from 76.8 g m^{-2} d^{-1}–1705.9 g m^{-2} d^{-1} (mean = 492.2 g m^{-2} d^{-1}) and are much higher than the values measured at Algar do Carvão. In the latter, values ranged from 0.3 g m^{-2} d^{-1}–2.3 g m^{-2} d^{-1} along the first survey (mean = 1.8 g m^{-2} d^{-1}) and from 5.7 g m^{-2} d^{-1}–8.1 g m^{-2} d^{-1} along the second survey (mean = 6.8 g m^{-2} d^{-1}) (Table 3).

Cumulative probability graphics were used to plot the data from the three surveys (Fig. 7). Only one lognormal population for each survey dataset was detected, suggesting only one CO_2 source for each dataset. The low values recorded in both surveys at Algar do Carvão, as well as the single population identified using the statistical approach (Fig. 7A and B), suggest a biogenic CO_2 source. The bulk $\delta^{13}C$ of dissolved carbonate in volcanic lakes is a function of the bulk $\delta^{13}C$ of the input term, and fractionations that may occur in a lake are a result of photosynthetic/biogenic activity (Varekamp, 2015). Further, in the dissolution process, an equilibrium fractionation between each carbon species and the interacting CO_2 takes places; therefore, the isotopic composition of the DIC represents the average weight of the isotopic compositions of all the carbon species and it cannot be representative of the isotopic composition of the gaseous CO_2 interacting with the water lake. Therefore, according to Zhang et al. (1995), we computed the isotopic composition value of the CO_2 gas in equilibrium with the lake water using the mass balance of the carbon species and the relative isotopic enrichment factors (ε). The isotopic composition of the DIC measured during the second survey in Algar do Carvão was −9.02‰, and the computed value of the CO_2 gas in equilibrium was −13.42‰. Therefore, this result suggests that a CO_2-fractionated biogenic source may be contributing to the water composition because it is depleted relative to the actual atmospheric value ($\delta^{13}C$ = −8.3‰; Clark, 2015).

A volcanic origin is attributed to the CO_2 released at Furna do Enxofre, where only a single population with high CO_2 flux was identified (Fig. 7C). However, a biogenic contribution cannot be excluded and is likely masked by the high measured CO_2 flux. The measured $\delta^{13}C$ value of the DIC was −2.49‰, and the computed $\delta^{13}C$ value of the CO_2 gas in equilibrium was −8.99‰, suggesting a prevailing magmatic origin ($\delta^{13}C$ in the range from −3.5‰ to −6‰ (Cartigny et al., 2001)) with a small contribution of CO_2 of organic origin.

Both surveys carried out at Algar do Carvão (Fig. 8A and B) show extremely low values without variations across the lake, resulting in a uniform and homogeneous pattern compared to the values at Furna do Enxofre (Fig. 8C). The pattern is more heterogeneous at Furna do Enxofre, with higher flux values measured in the central area of the lake. Nevertheless, the entire lake shows anomalously high values even though no bubbles were observed at the water surface, contrarily to other Azorean volcanic lakes where higher and deep-derived CO_2 fluxes were associated with visible bubbling at the surface (Andrade et al., 2016). The column water height in the central part of the lake may prevent observations of bubbling. The high degassing found at this lake, and in the cave soils in general, is likely associated with the N75E-trending inferred fault suggested by Hipólito (2009) (Fig. 8C).

The total amount of CO_2 emitted from the lake surface was estimated from the CO_2 flux maps, with values in the range from 0.32 (0.29–0.35) kg d^{-1} to 2.03 (1.98–2.10) kg d^{-1} for Algar do Carvão, corresponding to the Algar_1 and Algar_2 surveys, respectively, These are much lower values than those obtained for Furna do Enxofre, 6100 (5231–7420) kg d^{-1}. For comparison, these values were divided by the lake areas, resulting in a range of values from 1.5 t km^{-2} d^{-1} to 6.7 t km^{-2} d^{-1} for Algar do Carvão and 508.3 t km^{-2} d^{-1} for Furna do Enxofre. The latter estimate is higher than the one obtained in the Furnas lake (321 t km^{-2} d^{-1}), another water body in the Azores with anomalous mantle-derived CO_2 emissions at the surface, as identified by Andrade et al. (2016).

5. Conclusions

The first systematic study of CO_2 degassing in volcanic caves in the Azores was carried out in the Furna do Enxofre and Algar do Carvão lakes located on the islands of Graciosa and Terceira.

The major-ion relative composition is, in decreasing order, $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$ (Furna do Enxofre) and $Na^{+} > K^{+} > Ca^{2+} > Mg^{2+}$ (Algar do Carvão) for the cations and $HCO_3^{-} > Cl^{-} > SO_4^{2-}$ for the anions. Therefore, water from Furna do Enxofre has an Mg-HCO_3 composition, while samples from Algar do Carvão have an Na-HCO_3 composition, both being of meteoric origin. The EC values are as high as 632 μS cm^{-1} at Furna do Enxofre, suggesting a contribution from water–rock interactions, which explains the Mg enrichment.

The floating accumulation chamber method was used to perform CO_2 flux measurements along the lake surfaces, with 15 and 22

Table 3
Descriptive statistics for the CO_2 flux data and the partitioned CO_2 flux populations (Algar do Carvão: A1_AC – first survey, A2_AC – second survey and Furna do Enxofre: A_FE – single survey).

Population	Number of Points	Area (m^2)	CO_2 Source	Mean (g m^{-2} d^{-1})	Median (g m^{-2} d^{-1})	Minimum (g m^{-2} d^{-1})	Maximum (g m^{-2} d^{-1})	St. Dev. (g m^{-2} d^{-1})	Mean CO_2 90% Confidence Interval
A1_AC	15	179	Biogenic	1.8	1.7	0.3	2.3	2.7	1.65-1.96
A2_AC	22	299	Biogenic	6.8	6.8	5.7	8.1	0.6	6.65-7.05
A_FE	71	11950	Hydrothermal	492.2	395.0	76.8	1705.9	360.2	437.37–620.27

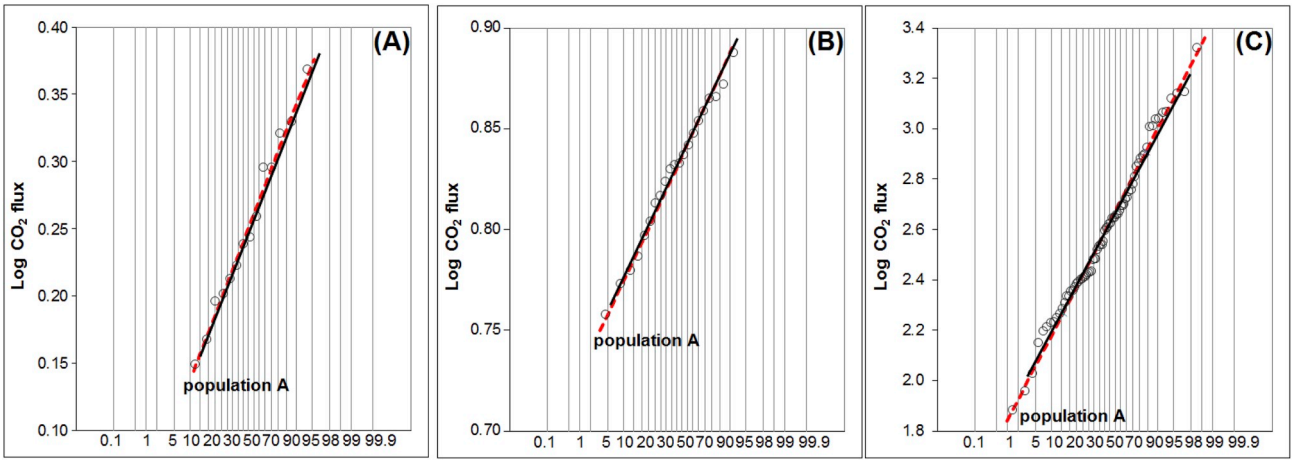

Fig. 7. Probability plots for the Algar do Carvão, (A) Algar_1 and (B) Algar_2, and (C) Furna do Enxofre CO_2 fluxes.

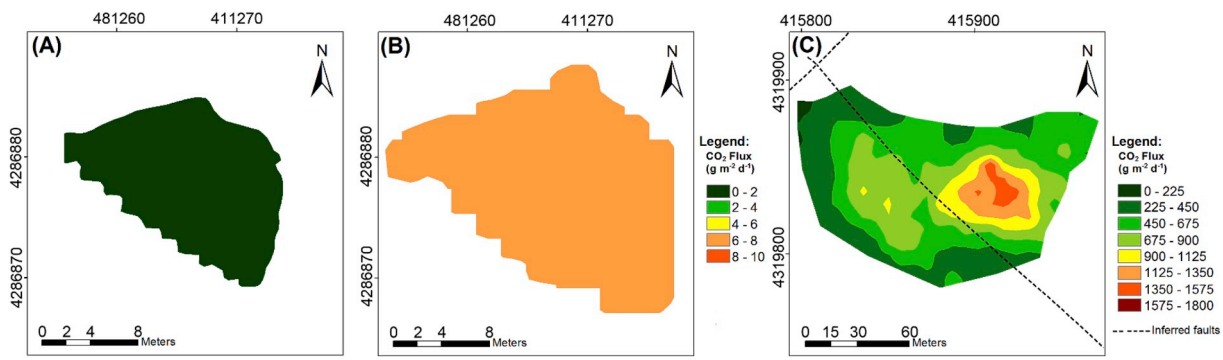

Fig. 8. CO_2 flux map for the Algar do Carvão and Furna do Enxofre lakes and the location of the main tectonic structures according to previous studies (Hipólito, 2009; Hipólito et al., 2013; Madeira et al., 2015): (A) Algar_1 (cell size = 2 m × 2 m; considering four neighbouring points); (B) Algar_2 (cell size = 2 m × 2 m; considering four neighbouring points) and (C) Furna do Enxofre (cell size = 7 m × 7 m; considering six neighbouring points).

sampling sites on Algar do Carvão and 71 sampling sites on Furna do Enxofre.

Based on the statistical approach defined by Sinclair (1974), a single CO_2 flux population was identified for the Algar do Carvão lake, representing a biogenic source, which is supported by the $\delta^{13}C$ values. Regarding Furna do Enxofre, only one population was statistically identified, pointing to a mantle-derived CO_2 source; no other lake was found in the literature with such a dominant volcanic-hydrothermal CO_2 origin. However, in the case of Furna do Enxofre, a biogenic source also contributes to the CO_2 emission as indicated by the $\delta^{13}C$ value of the CO_2 gas in equilibrium.

The CO_2 emission from Algar do Carvão shows a uniform and homogeneous pattern, while the Furna do Enxofre lake values are higher in the central area of the water body suggesting a higher permeability zone at the lake bottom. The high degassing found in this lava cave is likely associated with the tectonic structure previously suggested by Hipólito (2009).

Regarding the CO_2 output, the values in Algar do Carvão are very low (1.5–6.7 t km^{-2} d^{-1}) compared to those in Furna do Enxofre (508.3 t km^{-2} d^{-1}), which is fed by deeply derived CO_2. The results gathered in this study can be used to better constrain the carbon budget in active volcanic environments. In addition, at least on Graciosa, the results are also useful for the seismic and volcanic monitoring programmes developed on the island.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.02.006.

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