Surface CO₂ emission and rising bubble plumes from degassing of crater lakes in São Miguel Island, Azores

GLADYS MELIÁN¹,²,³*, LUÍS SOMOZA⁴, ELEAZAR PADRÓN¹,²,³, NEMESIO M. PÉREZ¹,²,³, PEDRO A. HERNÁNDEZ¹,²,³, HIROCHIKA SUMINO⁵, VICTOR H. FORJAZ⁶ & ZILDA FRANÇA⁶

¹ Environmental Research Division, Institute of Technology and Renewable Energies (ITER), 38611 Granadilla de Abona, Tenerife, Canary Islands, Spain.
² Instituto Volcanológico de Canarias (INVolCAN), 38400 Puerto de la Cruz, Tenerife, Canary Islands, Spain.
³ Agencia Insular de la Energía de Tenerife (AIET), 38611 Granadilla de Abona, Tenerife, Canary Islands, Spain.
⁴ Marine Geological Resources Division, Geological Survey of Spain (IGME), Rios Rosas 23, Madrid, Spain.
⁵ Geochemical Research Center, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-Ku 113-0033, Tokyo, Japan.
⁶ Observatório Vulcanológico e Geotérmico dos Açores (OVGA), Açores, Portugal.

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*Correspondence author, present address: Environmental Research Division, Instituto Tecnológico y de Energías Renovables (ITER), 38611 Granadilla, S/C de Tenerife, Spain. Tel: (34)-922-747700; Fax: (34)-922-747701, E-mail: gladys@iter.es
Abstract

We report in this paper the first detailed study on the types and distribution of active subaqueous fumaroles and surface diffuse CO\textsubscript{2} degassing, performed in the three main volcanic lakes of São Miguel Island (Sete Cidades, Fogo and Furnas), Azores archipelago, Portugal. The results of the surveys, carried out in May 2011 using a floating accumulation chamber and a dual beam 50 and 200 kHz echo sounder, revealed a very low surface CO\textsubscript{2} degassing at the three lakes, in the range 32-608 kg d\textsuperscript{-1}, but dense subaqueous degassing plumes located in the north of Furnas (7.5-9 plumes/100 m\textsuperscript{2}), with moderate density degassing in Fogo (1.5-2 plumes/100 m\textsuperscript{2}) and Sete Cidades crater lakes (1-1.5 plumes/100 m\textsuperscript{2}). The echo sounder detected hydro acoustic signatures interpreted as acoustic flares, “puffing” bubble plumes or walls of bubbles associated with numerous subaqueous fumaroles. The recorded echograms show the bubbles rise at speeds averaging between 19–30 cm/s at the bottom with frequencies of release from 1-2 to 31 s. Most subaqueous fumaroles are faded out by dissolution of CO\textsubscript{2} before reaching the lake surface. Dissolution processes are enhanced by the pH range observed in the three volcanic lakes (~7-9). Observed dissolved CO\textsubscript{2} values indicate that the pressure of this gas in the three lakes remained much lower than the hydrostatic pressure and the risk of alimnic eruption is negligible. We suggest that the rising levels of CO\textsubscript{2} sourced from the subaqueous bubbles could constitute a critical fuel for sub-surficial phytoplankton layers interpreted as horizontal acoustic plumes beneath the lake surface. The highest density of subaqueous degassing bubbling correlates with recent submerged secondary craters formed around the caldera rims of the three Late Quaternary stratovolcano complexes of São Miguel Island. Our results emphasize the need to perform regular surface degassing studies as an important volcanic surveillance tool in the Azores archipelago.
1. Introduction

Most of the world’s lakes are net sources of CO₂ to the atmosphere (Cole et al., 1994). This process is much more evident in the volcanic lakes, because they are major sites of emissions and condensation for volatile elements produced by magmatic activity. Recent estimates of global CO₂ emissions from volcanic lakes (~117 Mt/yr) show a similar value to recent estimated emissions for submarine and is equivalent to 30% of the global degassing of subaerial volcanism (Pérez et al., 2011). The main hazard in volcanic lakes is the accumulation of magmatic CO₂ that may result in the sudden release of enormous amounts of dissolved CO₂ gas trapped at the bottom of lakes. This process is well known by the scientific community after the Lake Monoun (1984) and Lake Nyos (1986) disasters, both in Cameroon (Sigurdsson et al., 1987; Le Guern and Sigvaldason, 1989; Kling et al., 2005; Kusakabe et al., 2008). Degassing at volcanic lakes occurs by an advective mechanism, in the form of ascending bubbles from active subaqueous fumaroles, and by molecular diffusion through the water-air interface. The latter is called diffuse degassing, and represents an important amount of the total CO₂ emission from volcanic lakes (Pérez et al., 2011). The magnitude of the diffuse CO₂ through the air-water interface depends on the concentration gradient between the air and the surface water.

Echo sounding methods have mainly been used on volcanic lakes for bathymetric purposes in Kawah Ijen Crater Lake, East Java, Indonesia, for example (Takano et al., 2004) or to map underwater volcanic structures in the Yellowstone Lake (Morgan et al., 2003). Due to the high contrast of acoustic impedance between water and the free gas phase, subaqueous fumaroles strongly scatter the acoustic energy in water (Greinert et
Echo sounding techniques also provided useful information on degassing rates and the carbon dioxide dynamics of the Kelud volcanic lake (Caudron et al. 2012). The Azores archipelago has 88 shallow lakes, most of which are associated with craters or subsidence calderas. This work presents the first results of diffuse CO$_2$ degassing and echo sounding surveys carried out in May 2011 at Furnas, Fogo and Sete Cidades volcanic lakes. These are the main volcanic craters of São Miguel Island, located in calderas of major stratovolcanoes where pre-historical and historical eruptions (between 1439-44 AD and 1630 AD) have occurred. The main goals of this work are: 1) to study the spatial distribution of diffuse CO$_2$ degassing; 2) to estimate the total output of CO$_2$ emitted into the atmosphere; 3) to analyze the types and distribution of active subaqueous fumaroles identified by means of a dual beam 50 and 200 kHz echo sounder; and 4) to study the possible CO$_2$ accumulation in the deep water in three main volcanic crater lakes of the São Miguel Island (Azores archipelago).

2. **Geological background**

Azores archipelago consists of nine volcanic islands, situated in the North Atlantic Ocean about 1,360 km west of continental Portugal. The geological setting of the Azores region is dominated by the role of the American, Eurasian and African lithospheric plate boundaries (Miranda et al., 2014). The most important tectonic structures recognized in the area are the Mid-Atlantic Ridge and the Terceira Rift. Together they are the main source of the seismic and volcanic activity recorded in the region (Lourenço et al., 1998). São Miguel (Fig. 1) is the largest and most populated island of the Azores archipelago and is located in the eastern part of the Terceira Rift. The island is formed by several volcanic edifices situated along a general E-W trend and is crossed by NW-SE, NE-SW, WNW-ESE and E-W regional tectonic structures (Trota, 1998). The recent volcanism of the São Miguel Island is related to three main volcanic
centers: Sete Cidades, Fogo and Furnas (Forjaz, 1984; Moore, 1991). During the last 5,000 years, the activity of these volcanic centers has resulted in at least 57 eruptive processes, with five eruptions during the past 500 years (Moore, 1991).

Volcano-hydrothermal fluid discharges in São Miguel are evident by the existence of low temperature fumaroles (95–100°C), steaming ground, thermal springs, cold CO₂-rich springs and areas of soil diffuse degassing (Viveiros et al., 2010). There are several thermal water discharges and cold-CO₂ enriched springs on São Miguel Island that discharge mainly from perched-water bodies and with a clear mantle CO₂ signature (Cruz & França, 2006).

The Sete Cidades volcano (350 m.a.s.l) is composed of a semi-circular crater slightly elongated along a NW-SE direction (5.2 x 4.8 km) with a total area of 18.5 km². Within the Sete Cidade crater, two separated crater lakes are aligned from SSW to NNE: the Lagoa Azul (Blue Lake) to the north and the Lagoa Verde (Green Lake) to the south (Fig. 1). The Lagoa Azul lake is slightly elongate along the NW direction (2.7 x 2.1 km) covering a total extension of 3.6 km². The Lagoa Verde is also an elongate lake (5.2 x 4.8 km) covering a total extension of 0.7 km². In this way, the two crater lakes cover around 25% of the Sete Cidades volcano crater. The caldera of Sete Cidades volcano formed approximately 22,000 years ago after the eruption of several cubic kilometers of trachyte pumice. Six vents are present on the floor of Sete Cidades caldera in a roughly circular pattern. Other vents may be submerged beneath Lagoa Azul and Lagoa Verde.

The youngest Sete Cidades intra-caldera eruption formed the Caldeira Seca pumice ring. It has a radiocarbon age of 500±100 years B.P. (Shotton & Williams, 1971) and correlates with a reported eruption at the time of Portuguese discovery of the island in the middle of the fifteenth century. Only two warm springs are known, near Mosteiros
on the northwestern coast and at Ponta da Ferraria on the western coast (Fig. 1). The
latter has a temperature of about 50°C (Moore, 1991).

Furnas volcano, a stratovolcano about 800 m a.s.l, occupies the east-central part of São
Miguel. The Furnas crater lake is located within the Furnas caldera, the third major
volcano of the São Miguel Island (Fig. 1). It is an elongate lake (2.0 x 1.5 km) covering
a total extension of 1.9 km². The geographical distribution of the water types in Furnas
caldera reveals a WSW–ENE lineament of volcanic CO₂ flux (Cruz et al., 1999). Furnas
volcano releases much more CO₂ in a non-visible or diffuse way (1,100 t d⁻¹; Viveiros
et al., 2010), than that released by water springs (4,556 t y⁻¹; Cruz et al., 1999), without
taking into account the contributions from fumaroles, bubbling pools, cold CO₂-rich
springs or Furnas lake. The Lagoa das Furnas is located at the western side of the inner
crater. During the last 5,000 years, at least 17 trachytic eruptions have taken place at
Furnas volcano, including 10 eruptions within the inner caldera that formed a trachyte
and pumice dome (Moore, 1991). Hot springs are prominent at Furnas volcano, the
distribution of which is shown by Zbyszewski et al. (1958). Those on the northern shore
of Lagoa das Furnas are probably related to the nearby caldera-bounding fault. Hot
springs in the village of Furnas are probably associated with the Furnas crater or with
radial fractures that formed during emplacement of the trachyte domes (Booth et al.,
1978).

The Lagoa do Fogo (“Fire Lake”) is a crater lake located in the inner part of the Agua
de Pau volcano, a stratovolcano with a prominent 3.0 x 2.5 km caldera with a total area
of 7.5 km² and walls as highs as 300 m (Fig. 1). At least five eruptions of trachyte
pumice have occurred from vents mostly within the inner caldera during the past 5,000
years (Booth et al., 1978). There have been two recent eruptions reported close to the
Lagoa do Fogo (Moore, 1990). The A.D. 1563 eruption formed low spatter ramparts on
top of Queimado, a relatively old trachyte dome about 6 km west-northwest of Lagoa do Fogo (Moore, 1990). In A.D. 1652, a strombolian eruption built a cinder cone and extruded flows about 10 km west of Lagoa do Fogo (Weston, 1964). Several hot springs, with temperatures commonly near boiling, are located on Agua de Pau, mainly on its northwestern flank (Zbyszewski et al., 1958). The hot springs suggest that hot rock or magma associated with the late Pleistocene and Holocene eruptions is close to the surface (Moore, 1991). Fogo volcano has developed an active geothermal system that is currently being exploited on its northern flank to produce over 100 GWh of electricity generated by geothermal power plants (Wallenstein et al., 2007).

3. Methods, analyzing and data processing

During May 2011, surface diffuse CO₂ efflux and echo sounder surveys were performed at Furnas, Fogo and Sete Cidades volcanic lakes, São Miguel Island. Diffuse CO₂ emission was measured in 102, 80 and 167 sampling sites selected at Furnas, Fogo and Sete Cidades, respectively to obtain an almost homogeneous pattern distribution, following the accumulation chamber method (Parkinson, 1981), with the chamber placed on a flotation device (Huttunen et al., 2003; Pérez et al., 2011). At each sampling site, pH, temperature and conductivity were measured at 15 cm depth from the water surface, by means of an Oakton pH/CON 300 meter. Spatial distribution maps were constructed using sequential Gaussian simulation (sGs) provided by the sgsim program (Deutsch & Journel 1998; Cardellini et al., 2003). The final maps were constructed as an average of 100 equi-probable realizations performed over a grid of 11,358, 4,836 and 3,967 squared cells (20m×20m) for Sete Cidades, Furnas and Fogo lakes, respectively, following spherical variogram models that honor the experimental variograms.

The echo sounder (ES) surveys were carried out by means of a Lowrance HDS-5 equipped with a dual frequency (50 and 200 kHz) transducer. Boat speeds range on
average between 0.5 and 3 knots. Digital data of the ES were processed by means of the
Sonar Viewer 2.1.2 software. Extracted bathymetric data were converted from the
Lowrance-type Mercator projection to Universal Transverse Mercator using ArcGIS
10.2. The bathymetric grid and 3D models of the crater lakes were generated using
Fledermaus IVS software. We used mainly the 50 kHz sampling frequency for the
analysis of the data, because data analyzed at 200 kHz missed bubbles that were
detected at 50 kHz, as demonstrated in Caudron et al. (2012). The calculating density
map of the acoustic plumes was constructed using the Kernel density procedure with
ArcGIS 10.2. This procedure calculates the number of plumes per unit of area from
using a kernel function to fit a smoothly tapered surface to each grid cell (i.e. 10 m).
Thus density of acoustic plumes is defined as the number of plumes per unit of area
(e.g. 150/km² or 1.5/100 m²).

To study the possible water stratification and CO₂ accumulation in the three volcanic
lakes, five vertical profiles of dissolved gas sampling were carried out (2 in Furnas, 1 in
Fogo and 2 in Sete Cidades). The vertical profiles were completed at the deepest point,
located after a short echo sounding survey. A 2.2 liters WaterMark horizontal PVC
water bottle was used to collect water samples at different depths. For each water
sample, chemical analyses were carried out in the laboratory. Cl⁻ and SO₄²⁻ were
analyzed by means of a Dionex DX-500 ion-chromatograph and HCO₃⁻ (main carbon
specie) was performed by automatic titration with a Metrohm 716 DMS Titrino. The
accuracy of the analysis was estimated at ~2-3 %. Dissolved He, N₂, CO₂(aq) and O₂
were analyzed following the method of Capasso & Inguaggiato (1998), with pure Ne as
host gas and a quadrupole mass spectrometer (QMS) Pfeiffer Omnistar 422. The
detection limit for He was estimated to be about 0.05 ppmV, while analytical accuracy
was approx. 2.5 % and 5 % for the main gas components and minor gas compounds,
respectively. Additionally, at the deepest point of each profile, isotopic composition of dissolved helium was also analyzed. Dissolved gases in these samples were extracted as explained by Padrón et al. (2013) and analyzed to determine helium and neon concentrations and helium isotopic ratios following the method of Sumino et al. (2001). Results are expressed as times $R_A$, being $R_A$ the atmospheric $^{3}$He/$^{4}$He ratio ($R_A=1.384 \times 10^{-6}$, Clarke et al., 1976).

4. Results and discussion

4.1 Sete Cidades crater lakes

4.1.1 Spatial distributions

Figure 2 depicts the spatial distribution of diffuse CO$_2$ emission (A), water pH (B) and temperature (C) values. Low diffuse CO$_2$ efflux values were measured at the water surface of Sete Cidades, ranging between non-detected values (<0.5 g m$^{-2}$ d$^{-1}$, 66 % of the data) and 4.1 g m$^{-2}$ d$^{-1}$. The highest values were measured mainly in the NW coastal areas of the Lagoa Azul (Fig. 2A). The diffuse CO$_2$ emission, computed to 608 ± 74 kg d$^{-1}$ released over an area of 4.5 km$^2$, represent one of the lowest normalized CO$_2$ emission rates (135 kg km$^{-2}$ d$^{-1}$) reported to date for a volcanic lake (Pérez et al., 2011). Surface water pH ranged in slightly basic values, between 7.1 and 9.1, with an average value of 8.1. A slight acidification (pH~7.6) can be observed in the water surface in the NW coastal area of Lagoa Azul, which suggests a relatively good spatial correlation between CO$_2$ emission and pH (Fig. 2B). In the case of water temperature, it ranged between 13.3 and 15.9°C, with an average value of 15.1°C, while air temperature was ~17°C. Warmer waters (>15°C) were observed in the middle of Lagoa Azul (Fig. 2C). Water conductivity showed an almost constant value around 113 $\mu$S/cm, without any significant spatial variability with a relative standard deviation (RSD) of 0.4%.

4.1.2 Vertical profiles
Two profiles were performed in Sete Cidades crater lake, one in Lagoa Azul and the other in Lagoa Verde, reaching 21 and 19 m depth, respectively (white star in Fig. 2). Both profiles showed a similar descending trend in the pH value from ~9 to ~7 (Fig. 3A), which indicates that dissolved CO$_2$ is mainly present as HCO$_3^-$ and CO$_2$(aq). Since the upper water layers in both profiles showed the most basic values (~9), eutrophication processes cannot be excluded. The descending trend in the pH is likely due to dissolution of CO$_2$ that is being released from the bottom of the lake. This process is more evident in Lagoa Azul. Figures 3B and 3F do not show any significant trend neither in the amount of HCO$_3^-$ nor in the total CO$_2$ dissolved in both Lagoa Verde and Azul. Bicarbonate values ranged between 30.6 and 39.3 mg/L (Fig. 3B). Total dissolved CO$_2$ (anionic CO$_2$ as HCO$_3^-$ plus CO$_2$(aq)) ranged between 36 to 53 mg/L (Fig. 3F). Slightly lower total dissolved CO$_2$ values (~20-30 mg/L) were reported by Cruz et al. (2006). However, there is no record of any increase in the CO$_2$ degassing rate over the period 2003-2011.

At the sites where the vertical profiles were performed, water temperature descended gradually with depth from ~16ºC at the surface to ~13ºC at the bottom for Lagoa Verde and the ~16ºC at the surface to ~15ºC at the bottom for Lagoa Azul (Fig. 3C), which indicates the existence of a dense stratification and rules out the possible existence of hot springs at depth at the sites where the profiles were made. A thermocline was not present in Sete Cidades lake. The deepest waters of higher ratios N$_2$/O$_2$ (higher than N$_2$/O$_2$ ratio in air-saturated water, ASW) were measured at the bottom of both Lagoa Verde and Azul, suggesting an addition of endogenous or biogenic nitrogen (e.g. benthic nitrogen production).
The $^3\text{He}/^4\text{He}$ ratio analyzed in the water of Lagoa Azul at 21 m depth (deepest point) showed a value similar to the atmospheric one, $0.95 \pm 0.04$ $R_A$, while in Lagoa Verde (19 m depth), the result was $0.67 \pm 0.04$ $R_A$.

4.1.3 Echo sounding results

4.1.3.1 Lagoa Azul crater lake

Figure 4A show the morphology of Sete Cidades crater lake. The bottom lake morphology of the Lagoa Azul is split into two different parts (Fig. 4B). The southern part is composed by a small circular depression, 450 m in diameter and 6 meter water depth (mwd), with flank slopes ranging between 3 and 4°. The northern part is composed by a stepped platform ranging from 5 to 22 mwd that ends in the north with a flat basin with 23-24 mwd (Fig. 4B). The platform and the deep basin are connected by an 8-9° steep slope. The deepest basin of the Lagoa Azul reaching 25 mwd is located close to the northern limit of the main crater of the Sete Cidades volcanic system (Figs. 1 and 4B).

Features of bubbles in echograms

The locations of the observed bubble plumes in the bottom of the lake are indicated as red dots in Figures 4, 5A and 5B. Most of the bubble plumes identified in the Lagoa Azul crater lake are located within the deep basin and along the steeped slope that connects the shallow platform (Fig. 4B). Except for the shallow parts, the north of Lagoa Azul exhibits frequent vertical plumes of bubbles (Figs. 5A and 5B). The bottom of the deep basin shows very concentrated zones that we termed as walls of bubbles (Fig. 5C). These walls or clouds sourced from the bottom lake form columns that span 190-225 m wide (Fig. 5C). The clouds that are only observed on the 50 kHz echogram are constituted by medium scattering values with numerous high backscattering small hyperbolas within the clouds when they are zoomed. High scattering crescent shapes
observed between the walls of bubbles are possibly related to a reduction of the speed of the boat from 3 to 0.5 knots expanding the shape of the targets and forming crescents. Most of the high density walls are sourced from the flanks of the steep slopes (Fig. 5C), reflecting possibly that active diffuse degassing is related to fault structures within the crater lake. A horizontal and strongly stratified 2-3 m thick layer showing very high backscatter values is extended over the subsurface of the deep basin of the Lagoa Azul at water depths ranging between 0.5 and 3 m (Fig. 5C).

Towards the border of the deep basin of the Lagoa Azul, the hydroacoustic manifestations of bubbling are identified as continuous streams of bubbles (e.g. Fig. 6A) and intermittent bursts of bubbles (e.g. Figs. 6B and 6C). The 50 kHz echograms of these bubble plumes illustrate the intermittency of the degassing process or puffing (Figs. 6B and 6C). Another characteristic of these bubble plumes is that they are also observed in the 200 kHz echogram as thinner plumes. Normally, data at 200 kHz miss bubbles that are detected at 50 kHz. The detection of these plumes by higher frequencies (with shorter wavelengths), reducing the range for observing targets, might indicate that they are formed by bubbles with greater diameters (Caudron et al., 2012).

**Density and distribution of plumes**

The density of plumes identified at Lagoa Azul show the maximum are located in the north of the lake (Fig. 5A). The calculated density of plumes reaches its highest values of 150 plumes/km² in the deepest basin of Lagoa Azul (Fig. 5B). The lake floor area of Lagoa Azul affected by bubbling plumes has an extension of 2.4 km² (Fig. 5B). This area with high density of bubbling plumes coincides with a certain rise in the lake surface water temperature up to 16°C.

**4.1.3.2 Lagoa Verde crater lake**
The morphology of the Lagoa Verde (Fig. 4C) is constructed of an asymmetric elongate (1.2 x 0.78 km) deep basin with the bottom located at 18-21 mwd at its southern side. The western flank of this basin is constructed of a stepped platform with water depths ranging from 4 to 18 m. In contrast, the eastern flank of the deep basin does not show such stepped morphology. The maximum slope of this crater lake averages 3-4° on the eastern flank of the deep basin. In this way, the bubble plumes identified in the Lagoa Verde are located along the deep basin and on the steep eastern flank of this basin (Fig. 5B).

Features of bubbles in echograms

The hydroacoustic manifestations of degassing in the Lagoa Verde crater lake are mainly constituted by bursts of bubbles and isolated flares (Fig. 5D). The bursts of bubbles are similar to those observed in the Lagoa Azul. These are composed of ascending trains of bubble plumes with their tops at approximately at 10, 7 and 6 mwd (Fig. 6D). These bubble plumes are sourced from 12 mwd and disappear at 6 mwd, indicating a rapid process of bubble dissolution in the water column. This process gives rise to high backscatter “walls” above the bubble plumes and beneath the subsurface horizontal layer. At these sites of degassing, the horizontal layer is thickened and “bright” very high backscatter spots are identified along the horizontal layer at the intersection with the disappearing rising bubble plumes (Fig. 6D). Isolated vertical plumes are also identified as acoustic columns that link the bottom of the lake to the horizontal layer (Fig. 5D). In contrast to bubble plumes, flares show slightly downward tapering cone shapes separated by 20 m width and 11-12 m height. One of observed difference between the burst of bubbles and isolated flares are that the latter are sourced from depressions of the lake bottom, indicating a source of diffuse and focused degassing respectively.
Density and distribution of plumes

The calculated density of plumes ranges between 125 and 150 plumes/km² with their maximum in the deepest basin of Lagoa Verde (Figs. 5B). The total area of lake floor of the Lagoa Verde affected by bubbling acoustic plumes is estimated to be 0.9 km² (Fig. 5B). As occurred in the Lagoa Azul, the pattern of the density maps point to degassing mostly throughout peripheral secondary craters within the main caldera complex (Fig. 5B). A third zone of moderate rate degassing (ranging between 50-75 plumes/km²) is located between the two lakes. This could be related to a small crater within the Sete Cidades caldera at the intersection with the NW-SE Mosteiro Graben (Figs. 1 and 5B). This is a pronounced structure on the northwestern flank of the caldera interpreted to be the sub-aerial segment of the Terceira Rift (Queiroz and Gaspar, 1998).

4.2 Furnas crater lake

4.2.1 Spatial distributions

Figure 7 depicts the spatial distribution of diffuse CO₂ emission values (A), water pH (B) and temperature (C). Similarly as was observed in Sete Cidades, low diffuse CO₂ effluxes values were measured at the water surface of Furnas, ranging between non-detected values (<0.5 g m⁻² d⁻¹, 82% of the data) and 13.9 g m⁻² d⁻¹. Although diffuse CO₂ effluxes were low, two considerable degassing sites can be identified (Fig. 7A): the shoreline near the Caldeira das Furnas hot springs, that occurs in the Furnas lake fumarolic field, with temperatures approaching boiling point of the gas-rich water at surface conditions (Cruz et al., 1999), and a site located slightly north of the center of the lake. Both sites were also characterized by the lowest surface pH values (Fig. 7B). Furnas lake fumarolic field is an anomalous diffuse CO₂ degassing structure with CO₂ emission values of more than 7 kg m⁻² d⁻¹ (Vivieros et al., 2010). The highest diffuse CO₂ emission values measured in the north of the lake are spatially correlated with this
diffuse CO$_2$ degassing structure. The diffuse CO$_2$ emission was estimated at 32 ± 11 kg d$^{-1}$ released by a surface of 1.9 km$^2$, which represents a lower normalized CO$_2$ emission rate (17 kg km$^{-2}$ d$^{-1}$) than that measured in Sete Cidades in this work. In the case of water temperature, it ranged between 13.9 and 15.6°C, with an average value of 14.9°C, while air temperature was ~17°C. No significant changes in surface water temperature were observed in Furnas Crater Lake (Fig. 7C). Spatial distribution of water conductivity is not shown because the values did not show any significant spatial variability, with an almost constant value of ~150 $\mu$S/cm with a RSD of 1.3%.

**4.2.2 Vertical profiles**

Two profiles were performed in Furnas crater lake, S-profile in the deepest part (pink star in Fig. 7) and N-profile close to the shoreline near the Caldeira das Furnas hot springs (white star in Fig. 7), reaching 9 and 5 m depth, respectively. No significant trend was observed in the pH of the waters (Fig. 3G). Water temperature data in both profiles indicate that the lake was not appreciably stratified during the study. The S-profile temperature values decreased with depth from ~15.6°C at the surface to 14.6°C at the bottom (Fig. 3I). This behavior was not present in the N-profile, where the water temperature showed an almost constant value around 15°C (Fig. 3I). The increase in the HCO$_3^-$ concentration with depth is more evident in the N-profile, where the higher CO$_2$ degassing rates were measured (Fig. 3H). Total dissolved CO$_2$ ranged between 40 to 58 mg/L (Fig. 3F). Cruz et al. (2006), reported an almost constant dissolved CO$_2$ value ~40 mg/L.

SO$_4^{2-}$ and Cl$^-$ concentrations were studied only in the S-profile. Although the concentrations of these anions were almost constant (Figs. 3J and 3K) throughout the profile, they reached the higher values at the bottom of the lake. Furnas showed the highest N$_2$/O$_2$ ratios in the deepest waters, suggesting an addition of endogenous or
biogenic benthic nitrogen production. The deepest waters of Furnas showed also
discrete enrichments in He (Fig. 3L). Assuming that helium concentrations in Furnas
Lake can be described by the concentration profiles observed (Fig. 3L), it is possible to
estimate the helium emissions through the water surface of Furnas by applying a pure
diffusive model. According to Fick’s law, the gas flux in the water surface is driven by
the concentration gradients along the depth and the diffusivity of the gas in water:

\[ F_i = -D_{i(w)} \frac{\partial C_{i(w)}}{\partial z} \]

being \( F_i \) the flux of \( i \) (kg m\(^{-2}\) s\(^{-1}\)), \( D_{i(w)} \) the diffusion coefficient in water (m\(^2\) s\(^{-1}\)), \( C_{i(w)} \) the concentration of \( i \) in water (kg m\(^{-3}\)) and \( z \) the depth (m). In the case of helium, we
used \( D_{He(w)} \) at the average temperature of Furnas Lake waters (15ºC), that is \(~5.45 \times 10^{-9}\)
m\(^2\) s\(^{-1}\). \( D_{He(w)} \) was calculated as an interpolation of the values between 10º and 20ºC
reported by Verhallen et al. (1984). The observed concentrations of helium at different
depths in both N- and S-profiles, were fitted with the following exponential decay
function:

\[ [He]_w = 1.58 \times 10^{-8} e^{-\left(\frac{z}{1.58}\right)} + 4.13 \times 10^{-7} \]

\[ [He]_w = 1.02 \times 10^{-7} e^{-\left(\frac{z}{1.02}\right)} + 5.45 \times 10^{-8} \]

for N- and S-profile, respectively. These fitting equations describe the helium
concentration (mg/L) in the water as a function of the depth (z). The derivative with
respect to depth at a \( z=0 \) (water surface) allows for the estimation of helium emissions
through the water surface (1.92 km\(^2\)) to be in the range of 8 to 20 mg d\(^{-1}\), with a
normalized emission value versus the area of 4.2-10.4 mg km\(^{-2}\) d\(^{-1}\). The \(^3\)He/\(^4\)He ratio
analyzed at 9 m depth (S-profile) was 1.12 ± 0.04 R\(_A\).

4.2.3 Echo sounding results
The maximum depth of the Furnas crater lake is 12 m located at its center (Fig. 8A). The slope of the lake flanks range from 9 to 12° whereas at its center the deepest basin shows slopes lower than 0.2°.

**Features of bubbles in echograms**

Subaqueous bubbling in the Furnas lake are identified as hydroacoustic `plumes` in the water column; i.e. strong backscatter signals 8-10 m height with a flare-like shape which are rooted to the lake floor (Figs. 8B and 9). Flares are mainly observed on the slope of the northern flank of the lake at water depths ranging between 5 and 12 m and are located close to the field of subaerial hot springs called Caldeiras das Furnas (Fig. 8A). Normally these flares ranging between 5 and 10 m in height reach the uppermost horizontal layer of high backscatter located at between 3 and 0.5 mwd (Fig. 8B). Most of the flares are sourced from the floor of the lake forming depressions or holes. (Fig. 8B), which show the same morphology as the nearby subaerial hot springs termed as “Caldeiras das Furnas” (Fig. 8B). The subaqueous “furnas” are characterized by 1-3 m deep 40-50 m wide lake floor depressions that are partially filled by recent sediments (Fig. 8B).

**Density and distribution of plumes**

Flares are mainly concentrated on the north basin of the Furnas crater lake around the area where the hot springs termed as the "Caldeiras da Furnas" are found (Fig. 8A). The density map shows the highest values of 750-900 plumes/km² in this area (Figs. 9A). However, the lake floor affected by this high density of plumes is only of 0.1 km². Other areas with moderate density ranging 350-400 plumes/km² are also observed in the center of the Furnas crater lake (Fig. 9A). Figure 9B shows 3D imaging of the flares rising from the bottom of the Furnas crater lake in the profiles C1 and C2 identified in
Figure 9A. At regional scale, the main density of flares identified at Furnas crater lake is located along the border of the caldera rim of the stratovolcanic complex.

4.3 Fogo crater lake

4.3.1 Spatial distributions

Figure 10 shows the spatial distribution of diffuse CO2 emission values (A), water pH (B) and temperature (C) at the water surface of Fogo Lake. Low diffuse CO2 effluxes are also shown, ranging between non-detected values (<0.5 g m\(^{-2}\) d\(^{-1}\), 63% of the data) and 3.8 g m\(^{-2}\) d\(^{-1}\). Highest values of diffuse CO2 emission (>2 g m\(^{-2}\) d\(^{-1}\)) were located in the south-east of the lake (Fig. 10A). Furthermore, the spatial variability of surface water pH and temperature was also very low: i.e. water pH and temperature fluctuated within the ranges of 7.0-7.3 and 12.4-12.9ºC, respectively. For this reason, a different color scale was used for their spatial distribution (Figure 10B and 10C) with respect to that used for Sete Cidades and Furnas lakes. The highest CO2 emission (~4 g m\(^{-2}\) d\(^{-1}\)) located in the south-east of the lake agreed with water temperature values (~13ºC). This is the reason why this locality was selected for the vertical profile (white star in Figure 10). The diffuse CO2 emission was estimated at 161 ± 14 kg d\(^{-1}\) released over an area of 1.59 km\(^{2}\), which represents a normalized CO2 emission rate of 101 kg km\(^{-2}\) d\(^{-1}\). Again, we do not show the spatial distribution of water conductivity due to the absence of considerable spatial variability, with an almost constant value of ~42 µS/cm with a RSD of 1.0%.

4.3.2 Vertical profiles

The profile performed in the south-east of Fogo crater lake reached 26 mwd (white star in Fig. 10). No significant trends were observed in any of the parameters analyzed in the profile (Figs. 3M-3R). Total dissolved CO2 values were the lowest of the three volcanic lakes studied in this work, and ranged between 7 and 8 mg/L (Fig. 3E), similar to values
reported by Cruz et al. (2006). No evidence of accumulation of CO$_2$ at the bottom of the lake was observed. It is worth noting that, although there were no vertical trends that allowed for the application of a diffusion model to estimate the emission of helium, important concentrations of this gas (up to 0.4 cm$^3$ STP/L) were measured at different depths (Fig. 3R). The $^3$He/$^4$He ratio analyzed at 20 m depth was 0.84 ± 0.03 RA.

### 4.3.3 Echo sounding

**Features of bubbles in echograms**

Two main types of hydroacoustic features related to bubbling have been identified in the Fogo crater lake (Fig. 11A): (i) scattered acoustic hyperbolas staggered up through the water column from the bottom of the lake and (ii) strong backscatter signal columns in the water column rooted to the lake floor. Two large hydroacoustic plumes have been identified in the southern basin of the Fogo crater lake (Fig 11B). These plumes are characterized by very high backscatter values forming 10 m high columns in the water column which are rooted to the lake floor and rise up 3 m below the lake surface (Fig. 11B). Both hydroacoustic plumes are connected throughout a strong backscatter horizontal signal 1-2 m below the surface of the lake.

**Density and distribution of plumes**

The map of density of acoustic anomalies of the Fogo lake show the highest spot of plumes with densities of 150-200/km$^2$, located in the north part of the Fogo crater lake (Fig. 11C). This high density bubbling spot covers a small zone of 0.158 km$^2$. At the same time, a zone of moderate plume density (averaging 75-100/ km$^2$) is also identified at the central and deepest part of the lake at water depths from 12 to 28 meters (Fig. 11C). In this sense, the map of density of plumes show a certain NW-SE trend which suggest they could be related to degasification along faults with this orientation (Fig. 11C). The location of the two bubbling plumes identified in the southern basin of Fogo
lake (Fig. 11B) coincides with the zone of increased diffuse CO$_2$ efflux $> 2$ g m$^2$ d$^{-1}$ (Fig. 10A) and also with a slight increase in the temperature of the water surface $>13^\circ$C (Fig. 10C).

**4.4 Subaqueous degasification characteristics of the São Miguel lakes**

Several types of hydroacoustic features are identified in the three studied crater lakes that we interpret in terms of sequences reflecting different types of bubbling by subaqueous degasification (Fig. 12). The two main end-members are: (i) the continuous streams of bubbling (flares and clouds) sourced from focused or diffuse sources and (ii) the intermittent bursts of bubbles (crescent shape hyperbolas). Flare-like plumes identified in Furnas are related to continuous streams of bubbles escaping from a focused source (Fig. 12A). The columns identified in the southern basin of Fogo are interpreted as continuous streams of bubbles but sourced diffusely (Fig. 12B). The cloud of bubbles sourced from the deep basin of the Lagoa Azul is interpreted as continuous streams of bubbles but sourced diffusely (Fig. 12C). These types of continuous streams of bubbling coincide with areas where a slight increase in surface temperature is observed as seen in the northern part of Furnas (Fig. 7C), the southern basin of Fogo (Fig. 10C) and the northern deep basin of Lagoa Azul (Fig. 2C). We suggest that these continuous plumes might be formed not only by degassing but also by the involvement of hydrothermal waters. Otherwise, intermittent degassing is identified as bursts of bubbles.

The velocity of the rise of bubbles can only be obtained from echograms in Sete Cidades crater lakes. In the case of continuous bubbling, the bubble rising speed can be directly measured by picking the time difference at two distinct depths (yellow and red circles in Fig. 6A) along the same ‘bubble-line’. The different slope of bubble-lines indicates distinct rising speeds (Fig. 6A). The progressive bending of a bubble-line
indicates a decrease in rise speeds due to bubble shrinkage (Greinert et al., 2006). The velocities of rise of continuous bubbling in the deep basin of the Lagoa Azul at 23 mwd range from 19 cm/s to 28 cm/s (Fig. 6A). This range of velocities falls within the typical range reported for rising bubbles (20 and 30 cm/s) with sizes between 5 and 20 mm in diameter, respectively (McGinnis et al., 2006). The upwards splitting and deceleration observed in bubble-line echograms (Fig. 6A) is interpreted as the result of breaking up of large bubbles into small ones or the effect of spatial divergence of a few close positioned bubbles that had been released from the bottom nearly simultaneously but could not be distinguished by the acoustic system (multiple targets) as proposed Ostrovsky (2003). When bubbles are not constantly released, the echograms show intermittent bursts of bubbles identified as “crescent shapes” (Figs. 6B, 6C and 6D). The occurrence of bubble bursts at the same water depth allows for the determination of frequencies at which bubbles are released from the lake bottom. From the calculation of the echograms, we observe that the main difference of degassing observed between the Lagoa Azul and Lagoa Verde is the frequency of release of the bubble bursts. The frequency of release in the Lagoa Verde (Fr=31 s) is much slower than the one observed in the Lagoa Azul (Fr=1.0-1.6 s) (Fig. 6). In the other crater lakes Fogo and Furnas, the crescent shape hyperbolas are much more smaller which makes the calculation of bubble release frequency not possible.

Echo sounding data revealed a high density of degassing acoustic plumes in the north part of Furnas crater lake (750-900/km²). In contrast, similar and moderate values of density of bubble plumes are calculated both in the deep basin of the Lagoa Azul (150/km²) and Lagoa Verde (125-150/km²), the north and south part respectively of Sete Cidades crater lake and Fogo crater lake (150-200/km²). The greatest area of lake bottom affected by degassing corresponds to 2.4 km² in the northern Lagoa Azul
whereas only 0.9 km² is affected in the southern Lagoa Verde. In Fogo crater lake, the extent of the main concentration of bubbling is very reduced (0.158 km²) and mainly concentrated in their southern basin. The lake bottom area affected by bubble plumes within the Furnas crater lake covers an small extent of 0.1 km², mainly concentrated on their northern part around the subaerial hot springs of Caldeira das Furnas.

The meaning of the horizontal acoustic plumes observed in the three crater lakes (Fig. 5C and 5D) is not explained by changes in the geochemical or physical signatures along the vertical profiles (Fig. 3). We suggest that this high backscatter layer could have biological origin related to the level of total dissolution CO₂ at the top of the bubble degasification plumes. In this way, the rising levels of CO₂ sourced from the bubble plumes could be a factor that triggers the intensification of phytoplankton blooms at this level as proposed by Verspagen et al. (2014). The eutrophication of Lake Furnas and Sete Cidades by large blooms of Cyanobacteria and microcystins has been recognized since the 1980s (e.g. Santos et al. 2005). We propose, thus, that the eutrophication acting as a “biological mask” might be the cause for the low CO₂ emission rates measured in the “latent” crater lakes. On the contrary, the observed columns of submarine degassing bubble plumes of CO₂ may trigger phytoplankton blooms at horizontal levels (e.g. Fig. 11B).

4.5. Hydrochemistry of the São Miguel lakes

We used the Cl-SO₄-HCO₃ ternary diagram to classify the Sete Cidades, Furnas and Fogo volcanic lake waters on the basis of the major anion concentrations (Giggenbach, 1991). Figure 13 shows the Cl-SO₄-HCO₃ ternary diagram including the data from Cruz et al. (2006). With the exception of Fogo, similar observations were made by Cruz et al. (2006), the dominant anion in the lake waters was HCO₃⁻. Although these waters are
located within a crater, they plot in the typical range defined for peripheral waters by Giggenbach, (1991).

In Figure 14, we show the $^{3}{\text{He}}/^{4}{\text{He}}$ versus $^{4}{\text{He}}/^{20}{\text{Ne}}$ diagram. The fact that $^{3}{\text{He}}/^{4}{\text{He}}$ and $^{4}{\text{He}}/^{20}{\text{Ne}}$ ratios of the Sete Cidades and Fogo lakes lie on the mixing line between atmospheric and crustal endmembers suggests that dissolved helium is mainly atmospheric with a possible minor addition of crustal (radiogenic) helium. These results indicate negligible mantle helium degassing at these lakes of São Miguel. At Furnas dissolved He showed a slight mantle origin, since it plots close to the air-MORB mixing curve (Fig. 14). The helium emission values are estimated for Furnas Lake (4.2-10.4 mg km$^{-2}$ d$^{-1}$) and is much lower than those soil diffuse helium emission values reported to date in other volcanic systems: Pico do Fogo, 2.8 x $10^{7}$ mg km$^{-2}$ d$^{-1}$ (Dionis et al., 2015); Cumbre Vieja volcano, 0.8-1.7 x $10^{5}$ mg km$^{-2}$ d$^{-1}$ (Padrón et al., 2012) and El Hierro Island, 0.3-1.4 x $10^{5}$ mg km$^{-2}$ d$^{-1}$ (Padrón et al., 2013). The differences are mainly due to the differences between the diffusion coefficient of helium in water (5.45 x $10^{-9}$ m$^{2}$ s$^{-1}$) and that for air (7 x $10^{-5}$ m$^{2}$ s$^{-1}$). The absence of a clear concentration gradient prevented the theoretical estimation of He emissions using Fick’s law in Fogo and Sete Cidades lakes.

The highest diffuse CO$_2$ emission rates coincided spatially with the highest density of bubbles in Furnas volcanic lake. The total CO$_2$ emissions were estimated from the floating accumulation chamber method, in the range 32-608 kg d$^{-1}$, represent some of the lowest CO$_2$ emission rates reported to date for a volcanic lakes (Pérez et al., 2011). In the case of Furnas, the emission value contrasts with the rest of Furnas volcano, which is considered one of the largest CO$_2$ emitting volcanoes, with a normalizing emission rate of ~186,000 kg km$^{-2}$ d$^{-1}$ (Viveiros et al., 2010). Andrade et al. (2016), reported recently a much higher CO$_2$ emission rate form the water surface of Furnas
(321,000 and ~28,000 kg km\(^{-2}\) d\(^{-1}\) for surveys performed in October-November 2013 and March 2014, respectively). This significant increase does not seem to be caused by the monomictic character of Furnas lake and should be attributed to changes in the volcanic activity of Furnas volcanic system. These results suggest that observed CO\(_2\) bubble plumes in the three volcanic lakes studied here dissolve almost completely and very rapidly, as has been observed in other volcanic lakes (Caudron et al., 2012). Echo sounding results confirm that most of the subaqueous fumaroles fade out by dissolution of CO\(_2\) before reaching the lake surface. The pH range observed in the three volcanic lakes (~7-9), and almost all total dissolved aqueous CO\(_2\) undergoes ionization in HCO\(_3^-\) and CO\(_3^{2-}\). Thus, dissolution processes also minimizes CO\(_2\) molecular diffusion through the water-air interface, reducing greatly the CO\(_2\) emissions towards the atmosphere. Emission rate values, normalized per unit area were very similar for Fogo and Sete Cidades (101-134 kg m\(^{-2}\) d\(^{-1}\)), and higher than that of Furnas (17 kg m\(^{-2}\) d\(^{-1}\)). This difference in one magnitude order may be due to the persistent advective discharge of volcano-hydrothermal gases through fumaroles and bubbling pools in Caldeira das Furnas that represent a preferred path for degassing. Since the isotopic composition of CO\(_2\) was not analyzed in this study, a biogenic CO\(_2\) emission cannot be ruled out and prevents to differentiation between a biogenic source and deep degassing. Even though most of these observed acoustic bubbles are related to only with CO\(_2\) degasification, the occurrence of hydrothermal waters in the vents is cannot be ruled out. Upward migration of water by thermal heating in some areas such as the deep basin of Lagoa Azul, southern Fogo and northern Furnas could explain the relative anomalies of the lake surface temperatures and the type of acoustic features. Therefore, the area with the highest density of bubbling in the Lagoa Azul (Sete Cidades) coincides (Fig.
4B) with the positive anomaly of temperature mapped on the lake surface waters (Figs. 2C). The northern area of the Furnas crater lake shows spots of anomalous temperatures and relatively low pH close to the subaerial hot-springs of Caldeiras das Furnas (Fig. 7). Furthermore, in this area flares are sourced from carved depressions within the lake bottom suggesting the movement of hydrothermal waters as formation process responsible for these erosional features (Fig. 8).

The present degassing at the three crater lakes has a close relationship with recent secondary craters formed around the caldera rim of the three Late Quaternary stratovolcano complexes of São Miguel (e.g. Moore, 1990): i.e. Sete Cidades, Fogo and Furnas. This is indicated by the dense population of acoustic plumes mapped within the lakes, shaped as sub-circular zones. Therefore, the shape of the highest density area of bubble plumes identified at Lagoa Azul and Lagoa Verde is formed in association with ring craters in a roughly circular pattern within the caldera rim of Sete Cidades (Fig. 5A). The same occurs in the Furnas crater lake where the main degassing activity is probably associated with a ring crater along the northern rim of the caldera of the Furnas stratovolcano (Fig. 8A).

5. Conclusions

In this work we analyzed the subaqueous degassing from the bottom of three crater lakes by means of a dual beam 50 and 200 kHz echo sounder as part of a multidisciplinary study. Data from the echo sounder has allowed for the detection of a wide range of intensities in the subaqueous degassing that we have classified into two categories: (a) continuous streams to intermittent bursts of bubbles and (b) focused to diffuse sourced degassing. Continuous stream of bubbles released from focused areas of the lake floor were identified as hydroacoustic flare-like shapes having high backscatter signals and rising up to the near surface of the lake. Examples of these focused
degassing flares up to 10 m-high have been detected in the northern basin of the Furnas lake close to subaerial hot springs and in the southern basin of Fogo. Continuous degassing but sourced from diffuse areas was identified as “clouds of bubbles”. This type of bubbling was observed mainly from the deep basin of the Lagoa Azul, rising up to 23 m into the water column. The rise speed of the bubble streams averaged 19-28 cm/s showing breaking up of large bubbles into small ones and deceleration on their way up from the bottom. Intermittent bursts, types of single/multiple bubbles (“puffing”) were identified as large crescent-like hyperbolas rising into the water column.

The frequency of bubble release ranged from 1-2 s in the Lagoa Azul to 31 s in the Lagoa Verde of Sete Cidades lake. The echograms show the bubble(s) ascent at speeds of 30 cm/s near the lake floor diminishing to 15 cm/s at mid-waters and fading by dissolution at c. 2 m below the lake surface. The degassing processes are mainly focused on secondary craters formed near the caldera rims of the three Late Quaternary stratovolcano calderas of São Miguel. Therefore, the highest density of subaqueous fumaroles we have mapped is c. 7.5-9 plumes per 100 m² within the northernmost basin of the Furnas caldera rim related to subaerial hot springs. Otherwise, we have measured a moderate density of subaqueous fumaroles as c. 1.5-2 plumes per 100 m² within the Fogo lake near the caldera rim of the Agua de Pau stratovolcano and c. 1-1.5 plumes per 100 m² within the deep basin of the Lagoa Azul lake located near to the caldera rim of the Sete Cidades stratovolcano.

Although there is an evident gas discharge from the bottom of the three lakes, observed dissolved CO₂ values indicate that the pressure of this gas in the three lakes remains much lower than the hydrostatic pressure and the risk of limnic eruption is negligible. Otherwise, the acoustic horizontal plumes that appear in the three crater lakes at 1-2 m
beneath the lake surfaces are related to subaqueous fumaroles but cannot be explained by changes in the geochemical or physical signatures along the vertical profiles. This high backscatter acoustic layer could have a biological origin related to CO₂ dissolution of the rising bubbles. Therefore, the CO₂ sourced from dissolution of rising bubbles enhanced by the pH range (~7-9) could be a factor that triggers the intensification of phytoplankton blooms at the subsurface of the lake as proposed by Verspagen et al. (2014). Eutrophication might act as a biological “mask” and thus, might explain the low surface CO₂ degassing measured at the three lakes, in the range 32-608 kg d⁻¹. Following this assumption, the elimination of this biological “mask” may suppose a drastic increase of CO₂ released to the atmosphere from this type of “quiescent” crater lakes (according the classification of Varekamp et al. (2000). Our results emphasize the need to perform regularly surface degassing and hydroacoustic studies as an important volcanic surveillance tool in the Azores archipelago. These studies are of special interest in the case of Furnas due to the recent significant increment in the emission rate of CO₂ reported by Andrade et al. (2016).

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References


GREINERT, J., ARTEMOV, Y., EGOROV, V., DE BATIST, M. & McGINNIS, D. 2006. 1300-m-high rising bubbles from mud volcanoes at 2080 m in the Black Sea:


Figure captions:

Figure 1. Map of São Miguel Island, Azores showing the location of Sete Cidades, Fogo and Furnas volcanic lakes.

Figure 2. Spatial distribution of surface CO$_2$ emission (A), water pH (B) and water temperature (C) values at Sete Cidades volcanic lake. Solid black dots and white star indicate sampling sites and vertical profiles locations, respectively.

Figure 3. Results of the physico-chemical parameters analyzed at different depths along vertical profiles in Sete Cidades (A-E), Furnas (G-L) and Fogo (M-R) volcanic lakes. F: Variation of total dissolved CO$_2$ with depth in Sete Cidades, Furnas and Fogo volcanic lakes, São Miguel. Symbols: Lagoa Azul: closed squares, Lagoa Verde: open squares, N-profile Furnas: closed circles, S-profile Furnas: open circles and Fogo: open triangles.

Figure 4. 3D bathymetric image of the Sete Cidades crater lake (A), Lagoa Azul (B) and Lagoa Verde (C). Red dots show the location of bubble plumes.

Figure 5. Location (A) and density map (B) of bubble plumes within the Sete Cidades crater lake. Echograms (50 kHz) of the Lagoa Azul (C) and Lagoa Verde (D) portraying well defined bubble plumes rising from the bottom of the lake, h = acoustic hyperbola. Color scale in C and D: green to yellow color reflects high concentration of bubbles (high scattering) and blue for low concentration (low scattering).

Figure 6. (A) Echogram (50 kHz) used to calculate the speed of the rising bubbles according the depth-time for each ‘bubble line’ in the Lagoa Azul crater lake. The red
and yellow dots indicate that bubbles rise at 19 and 28 cm/s respectively. (B) and (C) show echograms (50 kHz) illustrating the intermittency of the degassing process ‘puffing’ in the Lagoa Azul crater lake. Bursts of bubbles are emitted every 1-2 s. (D) and (E) show echograms (50 kHz) and interpretation respectively used to calculate the speed of rise of bubbles and the frequency of intermittent bubbling in the Lagoa Verde. Bursts of bubbles rise at velocities of 30 cm/s close to the bottom reducing their velocity to 15 cm/s as they ascend. The reduction in the rise velocities is related to the diminution of the bubble diameters as they dissipate. Bubble plumes disappear though the water column due to fast dissolution. Frequency of bubble bursts is obtained by calculating the time between two bubbles at the same water depth. In this case, the frequency between bubble bursts is 31 s. See text for further explanation.

Figure 7. Spatial distribution of surface CO₂ emission (A), water pH (B) and temperature (C) values at Furnas volcanic lake. Solid black dots and star (white: N-profile and pink: S-profile) indicate sampling sites and vertical profile locations, respectively.

Figure 8. (A) Location of bubble plumes within the Furnas crater lake. (B) Echogram (50 kHz) showing well-defined acoustic flares at the north side of the Furnas crater lake. Some plumes are rooted on depressions (‘furnas’) at the bottom of the lake.

Figure 9. (A) Density maps of bubble plumes in the north of Furnas crater lake. (B) 3D image of the flares rising from the bottom of the Furnas crater lake.

Figure 10. Spatial distribution of surface CO₂ emission (A), water pH (B) and temperature (C) values at Fogo volcanic lake. Solid black dots and white star indicate sampling sites and vertical profile locations, respectively.
Figure 11. (A). Location of bubble plumes and bathymetry of the Fogo crater lake. (B). Echogram (50 kHz) showing well-defined vertical bubble plumes linked by a horizontal plume beneath the surface of the lake in the southern basin of the Fogo crater lake. (C) Density maps of bubble plumes in the Fogo crater lake.

Figure 12. The sequence of acoustic features and their relationship with degassing processes in the studied crater lakes. The end-members are continuous vs. intermittent degassing and focused vs. diffused sources. Further explanation in the text.

Figure 13. Classification of waters from Sete Cidades, Furnas and Fogo volcanic lakes on the basis of relative Cl⁻, SO₄²⁻ and HCO₃⁻ content (in mg/L). Data from Cruz et al. (2006) are displayed as solid black symbols.

Figure 14. $^{3}$He/$^{4}$He vs. $^{4}$He/$^{20}$Ne diagram for dissolved gas from the bottom of Lagoa Azul, Lagoa Verde, Furnas (N- and S-profile) and Fogo crater lakes. Grey curves indicate calculated binary mixing lines between air saturated water (ASW), crustal ($^{3}$He/$^{4}$He = 0.01 RA) and mantle ($^{3}$He/$^{4}$He = 8 ± 1 RA, Graham, 2002) endmember compositions, having an assumed $^{4}$He/$^{20}$Ne ratio of $10^6$ and $10^3$ respectively.
Fig. 1

Fig. 2
Fig. 3
Fig. 12

Fig. 13

Fig. 14