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Title: Carbon dioxide diffuse emission and thermal energy release from hydrothermal systems at Copahue-Caviahue Volcanic Complex (Argentina)

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Abstract: The north-western sector of Caviahue caldera (Argentina), close to the active volcanic system of Copahue, is characterized by the presence of several hydrothermal sites that host numerous fumarolic emissions, anomalous soil diffuse degassing of CO2 and hot soils. In March 2014, measurements of soil CO2 fluxes in 5 of these sites (namely, Las Máquinas, Las Maquinitas I, Las Maquinitas II, Anfiteatro, and Termas de Copahue) allowed to estimate that ~165 tons of deeply derived CO2 are daily released. The gas source is likely related to a relatively shallow geothermal reservoir containing a single vapor phase as also suggested by both the geochemical data from the 3 deep wells drilled in the 1980's and gas geoindicators applied to the fumarolic discharges. Gas equilibria within the H-C-O gas system indicate the presence of a large, probably unique, single phase vapor zone at 200-210 °C feeding the hydrothermal manifestations of Las Máquinas, Las Maquinitas I and II and Termas de Copahue. A natural thermal release of 107 MW was computed by using CO2 as a tracer of the original vapor phase. The magmatic signature of the incondensable fumarolic gases, the wide expanse of the hydrothermal areas and the remarkable high amount of gas and heat released by fluid expulsion seem to be compatible with an active magmatic intrusion beneath this portion of the Caviahue caldera.

Cover letter

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Buenos Aires, 30 April 2015

Dear Editor,

We are pleased to submit to the Journal of Volcanology and Geothermal Research the paper titled "Carbon dioxide diffuse emission and thermal energy release from hydrothermal systems at Copahue volcano (Argentina)" by Giovanni Chiodini, Carlo Cardellini, María Clara Lamberti, Mariano Agusto, Alberto Caselli, Caterina Liccioli, Giancarlo Tamburello, Franco Tassi and Orlando Vaselli. All authors have actively contributed to this original work and have seen the final version of the submitted manuscript.

In the manuscript we present and discuss the results of the investigation of diffuse degassing in the north-western sector of Caviahue caldera (Argentina) close to the active volcanic system of Copahue. The area is characterized by anomalous soil diffuse CO_2 degassing, hot soils and fumarolic discharge. We estimated that ~165 tons of deeply derived CO_2 are daily released by a geothermal reservoir containing a single vapor phase with a temperature of ~200-215 °C, as suggested by the geochemical data of the fumarolic discharges and deep wells.

Using CO_2 as a tracer of the original vapor phase, a natural thermal release of ~110 MW was computed for the area.

The magmatic signature of the incondensable fumarolic gases, the large extension of the hydrothermal areas and the remarkable high amount of gas and heat released by fluid expulsion seem to be compatible with an active magmatic intrusion beneath this portion of the Caviahue caldera.

At our best knowledge, it is the first work on diffuse degasing in the area.

We are looking forward to hearing from you and should you need any further detail, please do not hesitate to contact us at the below reported coordinates.

Best Regards.

On the behalf of all the Authors,

Lic. María Clara Lamberti

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Dear Editor,

We thank you and both the reviewers for the positive comments to our work. The revised version takes into account all the suggestions of the reviewers.

It follows a point to point reply to the main reviewer comments.

Reviewer#1
The reviewer provided just a general comment and some corrections in the text. There are in our opinion some main points:

1) **Estimation of heat flux from soil temperature measurements** (i.e. the method of Fridriksson et al. 2006, and Dawson 1964). We note that this is an empirical method based on the comparison between soil temperature at 15 cm of depth and colorimetric measurements at the surface performed in New Zealand geothermal areas. Since the method is empiric and strongly affected by the soil properties it is not easily applicable to other areas. Furthermore Fridriksson et al (2006), who performed a comparison between the Dawson (1964) method and that based on the CO2 flux (i.e. the same we applied at Copahue) found a difference of about one order of magnitude and concluded: "*The discrepancy between the observed heat loss and the heat loss inferred from the CO2 emissions is attributed to steam condensation in the subsurface due to interactions with cold ground water.* ***These results demonstrate that soil diffuse degassing can be a more reliable proxy for heat loss from geothermal systems than soil temperatures.***"
For these reasons we did not apply the method based on soil temperature measurements but we qualitatively discuss the spatial correlations between CO2 flux and soil temperatures.

2) **Evaluation of potential future geothermal power production**
In our work we gave a detailed picture of the natural heat flux from the surveyed areas and this was one of the aims of our work. For instance, typically the energy conversion efficiency from thermal energy to electric is 0.1 (so the estimated heat release of 110 MW would return 11 MW, but this is a minimum estimation because most of the geothermal power plants exploit the thermal energy 'stored' in the fields and not just the natural flux). However we don't want enter in this topic because the eventual future geothermal power production will depend on many other engineering and political factors.

3) **Carbon isotopic composition of CO2 efflux**.
In the text we discussed this point highlighting that a better definition of the CO2 sources would have been done with the availability of isotopic data. The measurements were not performed mainly for logistical problems because the samples have to be analyzed in a short

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time (typically in a week) and this was impossible. As described in the text we used other methods to discriminate between background and hydrothermal-volcanic CO2 sources.

We followed most of the minor suggestions in the text, including Fig. 3 that was re-drawn to better highlight the measuring point location

Reviewer#2

This is a nice paper that quantifies CO2 and heat emissions from hydrothermal systems associated with the Copahue-Caviahue volcanic complex, Argentina. CO2 emissions were directly measured and heat emissions were inferred using CO2 as a tracer of the original vapor phase. The paper serves as a contribution to the global inventory on volcanic-hydrothermal CO2 emissions and, more locally, provides better understanding of the geothermal potential of the volcanic complex. Only minor changes are suggested.
Thank you

Specific comments:

1) I suggest changing "Copahue volcano" in the paper title to "the Copahue-Caviahue volcanic complex" to broaden the study site out.
Done.

2) Line 42: change "80's" to "1980's".
Done.

3) Line 44 and elsewhere throughout the text: I think "unique vapor zone" would be better described as a single vapor zone, i.e., "…indicate the presence of a single large vapor zone at 200-2100…"
We maintain the term 'unique' because it refers to the existence of only one large vapor zone feeding the degassing process. This, as explained in the text, is strongly suggested by the compositional homogeneity of the fumaroles collected from the different investigated sites.

4) Line 48 and elsewhere throughout the text: "large extension of the hydrothermal areas" would be better expressed as "wide expanse of…" or "wide spatial distribution of…"
Done.

5) The following parts of the Materials and methods section (3) belonging in the Results section: (1) lines 165-168; (2) Table1; (3) lines 203-205; (4) Table 2; Line 223; Line 248; (5)

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Table 3; (6) Table 4; (7) Lines 285-287.
We partly followed this suggestion: Table 1 and 2, where the analytical data and survey parameters are reported, were included in the material and methods section, while Table 3 and 4, where interpretative results are reported, were moved in the results section.

6) Throughout the Materials and Methods section, there seems to be quite a lot of descriptive text devoted to well-established methods that are already presented in the literature and could probably be cut from here. For example, could just Lines 181-183 be kept and Lines 184-201 be eliminated? Other methods descriptions could be trimmed as well.
We respectfully disagree with the reviewer because in our work we used instruments that were developed and set up in our laboratories. Those sentences are meant to describe the peculiar characteristics of these not-commercial instruments, which we think are of interest for the readers.

7) For consistency, I suggest moving subsection 3.3 up to 3.2 (after fumarole chemistry).
Done.

8) Figure 5 and page 18, paragraph 2: I find it rather difficult to see some of the spatial trends described in this paragraph in the soil CO2 flux maps. In some cases, I see linear features in the soil CO2 flux distributions, but in others, only round-ish blobs. Are all of the inferred faults on Figure 5 inferred based on the soil CO2 flux maps, or are some of them inferred based on previous geologic/structural studies? Please clarify. Also, I suggest loosening the language when describing the DDS geometries and their relationship to structural trends. For example, in Line 419: ""…are roughly consistent…" Line 423: "…roughly develop along…"
In our opinion the general structural control on diffuse degassing is quite evident (in particular in the largest surveyed areas, i.e. Thermas de Copahue and Las Machinas). However we followed the reviewer suggestion and we 'loosen' the language.

9) Figure 5: Because the grey stripes showing the extent of the "hot area" do not over lap on Termas de Copahue and Las Maquinas, it looks line these thermal areas are not located within this area. An outline around the hot area might show its extent more clearly.
Done.

10) Lines 432-434 and Lines 408-411: I would suggest stating early on in the Results section (when you move Table 1 to the Results and first describe it there) the observations that the compositions of fumaroles at Termas de Copahue, Las Maquinas, and Las Maquinas II are very similar, while Anfiteatro is different.
We did not move Table 1 and we think that the comment about the strong similarity among fumarole compositions is more incisive in this part of the text. Also in order to avoid repetitions we did not move these observations.

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11) Lines 472-477: Confusing- rewrite more clearly.
For typing error the same observation was repeated in 2 sentences. We corrected this error and we think that now the sentence is clearer.

12) Line 499: Change "subsoil" to "subsurface".
Done.

Once again, thank you very much for your time and assistance.

Best Regards,

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Highlights

- We mapped and quantified deeply derived CO_2 diffuse flux at Caviahue caldera
- About 165 t/d of CO_2 is released as diffuse degassing.
- The degassing is related to a geothermal reservoir containing a single vapor phase
- We computed a natural thermal release of 107 MW
- An active magmatic intrusion beneath the studied portion of the Caviahue caldera is suggested

CARBON DIOXIDE DIFFUSE EMISSION AND THERMAL ENERGY RELEASE FROM HYDROTHERMAL SYSTEMS AT COPAHUE-CAVIAHUE VOLCANIC COMPLEX (ARGENTINA)

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Highlights

- We mapped and quantified deeply derived CO_2 diffuse flux at Caviahue caldera
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Abstract

The north-western sector of Caviahue caldera (Argentina), close to the active volcanic system of Copahue, is characterized by the presence of several hydrothermal sites that host numerous fumarolic emissions, anomalous soil diffuse degassing of CO_2 and hot soils. In March 2014, measurements of soil CO_2 fluxes in 5 of these sites (namely, Las Máquinas, Las Maquinitas I, Las Maquinitas II, Anfiteatro, and Termas de Copahue) allowed to estimate that ~165 tons of deeply derived CO_2 are daily released. The gas source is likely related to a relatively shallow geothermal reservoir containing a single vapor phase as also suggested by both the geochemical data from the 3 deep wells drilled in the 1980's and gas geoindicators applied to the fumarolic discharges. Gas equilibria within the H-C-O gas system indicate the presence of a large, probably unique, single phase vapor zone at 200-210 °C feeding the hydrothermal manifestations of Las Máquinas, Las Maquinitas I and II and Termas de Copahue. A natural thermal release of 107 MW was computed by using CO_2 as a tracer of the original vapor phase. The magmatic signature of the incondensable fumarolic gases, the wide expanse of the hydrothermal areas and the remarkable high amount of gas and heat released by fluid expulsion seem to be compatible with an active magmatic intrusion beneath this portion of the Caviahue caldera.

1. Introduction

The poor knowledge of CO_2 fluxes released from natural sources, such as mantle and metamorphic reactions, is one of the most vexing problems in understanding the geological carbon cycle (Berner and Lagasa 1989). Large uncertainties affect the estimates of global CO_2 flux from volcanoes (Burton et al. 2013 and reference therein) due to the relatively limited flux measurements of volcanic plumes from persistently degassing volcanoes. In addition, the amount of CO_2 not directly related to volcanic craters and released from hydrothermal systems associated with most active volcanic regions is poorly constrained. Recently, an international initiative to fill this gap has been promoted by the scientific community with a project named DECADE (https://deepcarbon.net/content/deep-carbon-observatory-launches-decade-initiative), which supports investigations focused on the study of CO_2 fluxes from active volcanoes. The present study is in the framework of this initiative, being aimed at mapping and quantifying deep-originated CO_2, diffusively discharged from the hydrothermal areas located few kilometers east of the active volcanic system of Copahue (Patagonia, Argentina), where fumarolic discharges and large zones of soil diffuse gas emission occur. A second goal of this study is that to provide an estimation of the local geothermal potential.

The development of a quick and reliable technique for the measurements of soil CO_2 fluxes (Chiodini et al. 1998) has recently promoted applications in different fields of geological and environmental sciences. One of the most promising applications of this tool (namely, the accumulation chamber method) regards the use of soil CO_2 flux surveys for geothermal prospecting. This method allows to recognize and characterize CO_2 flux anomalies at the surface, which are caused by the circulation of hydrothermal fluids at depth. Soil CO_2 fluxes higher than those due to biologic activity are indeed commonly associated with the circulation of hydrothermal fluids (Chiodini et al. 1998; Cardellini et al. 2003; Lewicki and Oldenburg 2005). In addition, recent studies have shown that CO_2 diffuse degassing can provide important and reliable constraints for a correct evaluation of the geothermal potential from hydrothermal areas (Chiodini et al. 2005; Fridriksson et al. 2006; Werner and Cardellini 2006; Chiodini et al. 2007; Mazot and Taran 2009; Hernández et al. 2012; Rissmann et al. 2012; Bloomberg et al. 2014; Granieri et al. 2014; Dionis et al. 2015). In particular, the total budget of hydrothermal gases released at the surface can be used for a robust estimation of the minimum amount of geothermal fluids involved at depth in the degassing process. Consequently, the accumulation chamber method represents an effective, rapid and cheap instrumentation for estimating the minimum geothermal potential of an unknown area since the thermal energy naturally transported and released by the fluids can be evaluated.

2. Geological, volcanological and hydrothermal setting

The Copahue-Caviahue Volcanic Complex (hereafter CCVC, 38°S-71°W) is located in the Neuquén Province (Patagonia, Argentina) on a segment of the Andes range, called the South Volcanic Zone (hereafter SVZ: 33.3° - 46°S), 30 km east of the main Pleistocene-Holocene volcanic front (Fig. 1). Volcanism in the SVZ is related to the subduction of the Nazca Plate beneath the South American Plate, at rates as high as 10.8 cm y^{-1} (DeMets et al. 1994; Ramos and Folguera 2000; Melnick et al. 2006).

Figure 1. a) Geological, volcanological and structural setting of the Copahue-Caviahue Volcanic Complex and location of the study area (modified from Folguera et al. 2004); b) location of the surveyed hydrothermal sites.

The steepening of the oceanic plate subducted in the last 5 Ma resulted in the displacement of the astenospheric wedge and an astenospheric upwelling. This process favored a process of crustal thinning that caused the most recent westward migration of the volcanic arc, extensional dynamics and large effusions of basaltic-andesitic magma (Folguera et al. 2006; Yuan et al. 2006).

The CCVC includes the Caviahue Caldera (also known as Caldera del Agrio), a volcano-tectonic depression defined as an intra-arc extensional pull-apart basin (Ramos and Folguera 2000; Bermúdez et al. 2002; Melnick et al. 2006; Rojas Vera et al. 2010). The pull-apart basin is located at the transition zone between the Liquiñe-Ofqui dextral-slip and the Antiñir-Copahue fault systems (Lavenu and Cembraro 1999, Folguera et al. 2004). The former accommodates lateral displacements imposed by the oblique convergence between the Nazca and South American plates from ~46°S to ~38°S (Radic 2010). The CCVC encompasses the Copahue volcano, a Pleistocene polygenic stratovolcano located in the southwestern rim of the Caviahue Caldera, whose main products are andesites and basalts (Polanco 2003). The easternmost of the nine NE-oriented summit craters of the Copahue volcano is currently active. During the last 250 years, at least thirteen low-magnitude phreatic and phreatomagmatic eruptions occurred from this crater (Martini et al. 1997; Naranjo and Polanco 2004). The 1992 and 1995 eruptions mostly consisted of phreatic events characterized by the emission of pyroclastic sulfur. In 2000, a phreatomagmatic eruption, mainly involving juvenile material, occurred (Delpino and Bermúdez 1993; 2002; GVN 2000a; 2000b). Since November-December 2011, the discharge rate of fluids from the Copahue active crater increased, whereas sporadic phreatic events have been occurring since July 2012. A major phreatomagmatic-magmatic eruption was observed on December 22, 2012 and a significant degassing is still ongoing (Caselli et al. 2015).

During quiescent periods, the active crater hosts a hot acidic lake (up to 63 °C and pH<1) (Varekamp et al. 2001; 2009; Agusto 2011; Agusto et al. 2012; 2013). Two acidic hot springs (up to 80 °C and pH = 1-2) discharge in the eastern summit flank of the cone and merge downstream to form the upper Agrio river (pH = 2-3), which flows into the acidified glacial Lake Caviahue (Martini et al. 1997; Gammons et al. 2005; Varekamp et al. 2008; Caselli et al. 2005; Agusto 2011; Agusto and Varekamp 2015).

In March 2014, a remote sensing campaign, carried out by combining MiniDoas and Multigas techniques, revealed the presence of an important gas plume from the crater lake and allowed a rough estimation of the released SO_2 and CO_2, which resulted to be of ~960 and ~640 ton d^{-1}, respectively (Tamburello et al., 2015).

In the north-eastern flank of the Copahue volcanic edifice, within the Caviahue Caldera, six hydrothermal areas are recognized: Las Máquinas, Las Maquinitas I, Las Maquinitas II, Anfiteatro, Termas de Copahue and Chancho-Co (Mas et al. 1996; 2000; Fig. 1). The hydrothermal activity of some of these sites (Las Máquinas, Las Maquinitas and Termas de Copahue) is so intense that causes a background volcanic tremor as revealed by a seismic array analysis performed in the 2003-2005 period (Ibañez et al. 2008). Fluids are discharged as boiling, bubbling and mud pools (up to temperatures of 96 °C), fumaroles (up to 130 °C at La Maquinitas I) and larges areas of diffuse degassing and hot soils. According to the recent, comprehensive study of the hydrothermal-volcanic fluids at CCVC by Agusto et al. (2013), the fumarole chemistry suggested that the gas source was associated with boiling processes of a hydrothermal system, mainly fed by meteoric water, although affected by magmatic fluids of mantle signature, as indicated by the relatively high $^3He/^4He$ ratios (R/Ra >7).

3. Material and methods

3.1 Sampling and analysis of gas from fumaroles

Fumarolic discharges from the thermal areas of Las Máquinas, Las Maquinitas I and II, Termas de Copahue and Anfiteatro were collected in March 2012 by using pre-evacuated flasks containing a 4N NaOH solution (Giggenbach 1975; Giggenbach and Gouguel 1989) for the analysis of the major gas species. Vapor condensates and, separately, dry gases were sampled using a condenser, cooled at ~20–30 °C by cold water. The chemical analyses were carried out at Osservatorio Vesuviano (INGV) laboratories. The gas chemistry of non-absorbed gases, present in the headspace over the NaOH solution, was determined by gas chromatography through a unique injection on two molecular sieve columns (MS 5 Å capillary, 30 m × 0.53 mm × 50 μm; He and Ar as carrier gases) using TCD detectors. Carbon dioxide and sulfur species absorbed in the alkaline solution were analyzed after oxidation via H_2O_2, by acid–base titration and ion chromatography, respectively (analytical error ±3%). Because of reaction in alkaline solution to form $COOH^-$ (Giggenbach and Matsuo 1991), CO was analyzed on dry gas samples by gas chromatographic separation with a MS 5 Å 1/8 × 50 in column (He as carrier gas) coupled with a high-sensitivity Reduced Gas Detector (HgO). The analytical results are reported in Table 1. In the Table 1 the $^3He/^4He$ isotopic ratios, expressed as R/Ra where R is the measured $^3He/^4He$ ratio and Ra is that of air (1.39×10^{-6}), are from Agusto et al. (2013).

Table 1. Chemical composition of the fumaroles of the surveyed areas (March 2012). Gas concentrations are expressed in μmol/mol, helium isotopes as R/Ra ($^3He/^4He_{sample}/^3He/^4He_{air}$). Equilibrium temperatures were calculated within the H_2O-H_2-CO_2-CO-CH_4 gas system ($T_{H\text{-}C\text{-}O}$; Tassi et al., 2015) and the geothermometer based on the CO/CO_2 ratio ($T_{CO\text{-}CO2}$; Chiodini et al., 2015).

3.2 Fumarolic flux

A well defined gas plume, suitable for the determination of the CO_2 flux discharged by the fumarolic vent, was found at Las Maquinitas I. Here, the technique proposed by Aiuppa et al. (2013) was applied. The method consists on the measurement of the Integrated Column Amount (ICA, kg m^{-1}) of CO_2 that is subsequently multiplied by the plume transport speed (m/s) to calculate the flux. The concentration in the plume of CO_2, as well as that of other gases (not discussed here), was measured with a portable MultiGAS system (Aiuppa et al. 2013 and references therein) along the horizontal and vertical axes of an orthogonal cross-section of the plume. During the measurements the plume was sub-horizontal as the wind was blowing to the East with constant speed. We calculated the average CO_2 concentration of ~90 samples (0.5 Hz sampling rate) every meter on an 8 m long horizontal axis, and every 0.4 m on a 2.4 m high vertical axis. The gas velocity was determined by tracking the transport speeds of individual gas puffs on a video recorder with a Nikon D90 video camera. The measured plume speed of 6.9 ± 2.2 m s^{-1} leads to a CO_2 flux of 3.2 ± 1.1 t d^{-1}.

3.3 Soil CO_2 flux and temperatures

Soil CO_2 flux (ϕCO_2) and temperatures (1,763 measurements) were measured at Las Máquinas, Las Maquinitas I and II, Anfiteatro, and Termas de Copahue (total investigated area = 1.21 km^2; Fig. 1b). The degassing area of Chancho-Co was not investigated due to logistical problems.

Soil CO_2 fluxes (ϕCO_2) were measured using two accumulation chamber devices developed and calibrated at the laboratories of Osservatorio Vesuviano and University of Perugia. The two equipments, operating in a dynamic mode as described in Chiodini et al. (1998), consist of: 1) a metal cylindrical vessel (the chamber, AC), 2) an Infra-Red (IR) spectrophotometer, 3) an analog-digital (AD) converter, and 4) a palmtop computer. The AC has a volume of ~2.8 L and is equipped with a ring-shaped perforated manifold re-injecting the circulating gas to ensure the mixing of the air in the chamber. The IR spectrometers consist of LICOR Li-800 and LICOR Li-820 detectors equipped with sensors operating in the range 0-20,000 ppm of CO_2. The soil gas circulates from the chamber to the IR sensor and vice versa by a pump (~1 L min^{-1}). The CO_2 concentration inside the AC is acquired every 250 msec. The signal is converted by the AD and transmitted to a palmtop computer, where a CO_2 concentration vs. time diagram is plotted in a real time. The ϕCO_2 is computed from the rate of CO_2 concentration increase in the chamber (dC_{CO2}/dt), according to the following equation:

$$\phi CO_2 = cf \times dC_{CO2}/dt. \qquad (1)$$

The proportionality factor (*cf*) between dC_{CO2}/dt and ϕCO_2 was determined before the survey during laboratory tests. The ϕCO_2 values, typically from 10 to 10,000 g m^{-2} d^{-1}, were measured on a "synthetic soil" made of dry sand (10 cm thick) placed inside a plastic box with an open top. The *cf* factor was then computed as the slope of the linear best-fit ϕCO_2 vs. dC_{CO2}/dt straight line.

Soil temperature was measured at the depth of 10 cm by means of a thermocouple equipped with a metallic probe.

The extension of the five surveyed areas, together with the number and the range of the CO_2 flux (ϕCO_2) measurements for each area, are reported in Table 2. The complete set of the ϕCO_2 data is available in the supplementary material (SM1).

Table 2. Main parameters of the five surveyed areas.

3.4 Soil CO_2 fluxes and temperatures data processing

The ϕCO_2 data were used to compute the total CO_2 release from the deep volcanic-hydrothermal source and to map its spatial distribution, as well as that of the soil temperature, by applying the Graphical statistical approach (GSA) and the sequential Gaussian simulations (SGS) methods.

Soil CO_2 flux values in hydrothermal areas are characterized by complex statistical distributions, which generally reflect the coexistence of different CO_2 sources such as biogenic and endogenous (Cardellini et al. 2003). In a logarithmic probability plot, where a straight line describes one log-normal population, these complex distributions result on a curve with *n* inflection points, which describes the overlapping of *n+1* log-normal populations.

The GSA method (Chiodini et al. 1998) was used to both partitioning these distributions into the individual log-normal populations and estimating their proportion (f_i), mean value and standard deviation. The partition was performed according to the graphical procedure proposed by Sinclair (1974). Since the computed statistical parameters of the populations (i.e. mean and standard deviation) refer to the logarithm of values, the mean value of ϕCO_2 (M_i) and the central 90% confidence interval of the mean were estimated by means of a Montecarlo procedure. The estimated mean flux values were used to compute the CO_2 released from the investigated areas and associated with each population by multiplying M_i by the respective covered surface (S_i), the latter being assumed as a fraction of the total surveyed area (S), which corresponds to the relative proportion of the population (i.e. $S_i = f_i \times S$). The total CO_2 release from the entire area can then be obtained by summing up the contribution of each population (i.e. $\Sigma f_i \times M_i \times S$). Similarly, the central 90% confidence interval of the mean value was used to calculate the uncertainty of the total CO_2 output estimation of each population.

Although the GSA approach is a useful tool for the interpretation of the diffuse degassing process, the results obtained by this method can be affected by some arbitrary choices, as follows: i) the polymodal log-normal distribution of CO_2 flux values is a convenient model for subsequent partitioning. Nevertheless, the statistical distribution of the CO_2 flux can be more complex than that of a simple log-normal distribution, ii) the partitioning procedure does not imply a unique solution, iii) the spatial distribution of the measured values is not considered by this statistical approach, and iv) the interpretations of the CO_2 flux distribution at the tails, especially for high flux values, can highly be affected by a low number of measured values. As a consequence of the latter "choice", the estimate of the total CO_2 output can be subjected to remarkable differences.

An alternative and more reliable estimation of the total CO_2 output can be obtained from the CO_2 flux mapping by the Sequential Gaussian Simulation (SGS) algorithm provided by the sgsim code (Deutsch and Journel 1998). According to Cardellini et al. (2003) and Lewicki et al. (2005), SGS yields a realistic representation of the spatial distribution of the CO_2 fluxes reproducing the histogram and variogram of the original data.

The SGS method produces numerous equiprobale and alternative simulations of the spatial distribution of the attribute, i.e. CO_2 flux and temperature in this work. Since the SGS procedure requires a multi-Gaussian distribution, original data were transformed into normal distribution by a normal score transform (Deutsch and Journel 1998; Cardellini et al. 2003). Experimental variograms of the normal scores were computed and modeled for each data set. The models were used in the SGS procedure to create 200 simulations of the normal scores. The simulated normal scores were then back-transformed into values expressed in original data units, applying the inverse of the normal score transform. The average of the values simulated at each cell of the grid in the 200 simulations were used to draw the maps of soil CO_2 flux and soil temperature. For each simulation the total CO_2 release was computed by summing up the products of the simulated value of each grid cell by the cell surface. The mean and the standard deviation of the 200 values of total CO_2

output were assumed to be the characteristic values of the CO_2 release and of its uncertainty, respectively, for each surveyed area.

4. Results and discussions

4.1 CO_2 soil degassing

The investigated areas were characterized by a wide range of CO_2 flux values, which varied from <0.05 g m^{-2} d^{-1} to >16,560 g m^{-2} d^{-1} (Table. 2). Each data set is reported in the logarithmic probability plots of Figure 2. These diagrams show the results of the GSA analysis, which includes i) the partitioned log-normal populations (blue straight lines), ii) their proportion, mean and standard deviation, and iii) the theoretical statistical distribution resulting from the combinations of the individual populations (red dashed curves).

The proportion, mean and standard deviation and the total CO_2 output calculated for each population are reported in Table 3.

Figure 2. Probability plots of Log ϕCO_2 for the different hydrothermal sites and partition of the distributions in log-normal populations (blue lines).

Table 3. Estimated parameters and partitioned populations in the 5 surveyed areas.

On the basis of the mean flux values characterizing the different populations, an interpretation of the main CO_2 source is reported in Table 3. “Background” refers to CO_2 fluxes related to soil respiration, whereas the term “endogenous” is related to those fluxes fed by volcanic-hydrothermal degassing. The latter includes those populations characterized by high mean ϕCO_2 values, typically in the order of 10^3 g $m^{-2}d^{-1}$, i.e. much higher than those produced by biogenic sources in the soil, which typically are 2-3 order of magnitude lower (e.g., Raich and Schlesinger 1992; Raich and Tufekcioglu 2000; Cardellini et al. 2003). At Las Máquinas, Anfiteatro and Termas de Copahue, the distribution of the CO_2 flux values in the probability plots indicates the presence of more than one “background” population (Table 3). The occurrence of different background populations possibly reflects the presence of different soils and vegetation in the surveyed areas. The background populations with the lowest mean values of ϕCO_2 (normally <1 g m^{-}

$^{2}d^{-1}$) correspond to fluxes from bare altered soils. Such low values could nevertheless be referred to an endogenous source, although their origin cannot properly be assessed since no isotopic carbon values of the CO_2 efflux (Chiodini et al., 2008) are available. However, it is to be pointed out that contributions by low flux populations to the total CO_2 budget are negligible. The relatively high ϕCO_2 values, which characterize the background populations "B" at Las Máquinas (24 g $m^{-2}d^{-1}$), C at Anfiteatro (26 g $m^{-2}d^{-1}$), and B at Termas de Copahue (22 g $m^{-2}d^{-1}$), are mainly representative of the presence in the surveyed areas of wet soils and peat (Table 3).

The estimated total CO_2 outputs using the GSA approach, i.e. the sum of all contributions from the different populations, range from 4.4 t d^{-1} (Las Maquinitas I) to 119 t d^{-1} (Termas de Copahue). The central 90% confidence interval of the mean value is generally large and, especially at Anfiteatro and Las Maquinitas II, it varies of one order of magnitude (11-110 t d^{-1} and 4-44 t d^{-1}, respectively). These large uncertainties mainly depend on the relatively low number of samples available for the definition of the high-flux populations, which mostly contribute to the total CO_2 output. On the contrary, the computations of the background populations are affected by a lower uncertainty because they are less variable and are defined by numerous samples (Fig. 2, Table 3). Assuming that CO_2 of the background populations is totally derived from shallow biogenic sources (soil respiration, e.g. Raich and Schlesinger 1992), the total background CO_2 output is of 5.9 t d^{-1} at Las Máquinas, nil at Las Maquinitas I, 0.09 t d^{-1} at Las Maquinitas II, 3.3 t d^{-1} at Anfiteatro and 9.2 t d^{-1} at Termas de Copahue.

In order to map the CO_2 fluxes and to compute the total gas release using the SGS approach, experimental variograms of the normal scores of the data were computed and modeled for each data set (Table 4). The models were used in the SGS procedure to create 200 simulations of the CO_2 flux according to the computation grids described in Table 4. The obtained CO_2 flux maps are reported in Figure 3.

Table 4. Relevant parameters of SGS application and estimation of the total CO_2 output from Copahue hydrothermal sites.

All the surveyed areas are characterized by a well-defined Diffuse Degassing Structure (DDS), except at Anfiteatro where the CO_2 fluxes are less spatially organized.

Figure 3. Maps of the CO_2 flux for the different hydrothermal sites (map coordinates are expressed in m, UTM-WGS84 19S).

The total SGS-computed CO_2 release ranged from 5 t d^{-1} (Las Maquinitas I) to 100 t d^{-1} (Termas de Copahue) with a relatively low uncertainty (≤10%; Table 4). These values can be considered comparable with those obtained by the GSA approach, except for Las Maquinitas II and Anfiteatro, where the SGS estimates are about 50% less than those obtained by GSA. These differences are likely related to an overestimation computed by GSA because a relatively low number of CO_2 flux measurements are available for the definition of the high flux populations. For this reason, the total CO_2 release obtained by the SGS approach was preferred for further computations.

The amount of released endogenous CO_2 (Q_{CO2}) was computed for each area by subtracting the specific background contribution estimated by GSA to the total CO_2 release estimated by SGS. The computed Q_{CO2} varies from 5 t d^{-1} (Las Maquinitas I) to 90.8 t d^{-1} (Termas de Copahue) (Table 4).

4.2 Soil temperature distribution

The soil temperature maps obtained by applying the SGS algorithm are reported in Figure 4 and refer to the temperature at 10 cm depth, concurrently measured with each ϕCO_2 measurement.

Setting aside Anfiteatro, the soil temperature spatial distribution (Fig. 4) in the investigated areas closely mimics that of ϕCO_2 (Fig. 3). A correlation between soil temperature and ϕCO_2 is not surprising because the presence of fumarolic emission favors a massive steam condensation at shallow depth, heating the soil by the latent heat of condensation and causing a flux of incondensable gases (i.e. mostly CO_2) toward the surface (Chiodini et al. 2001; 2005). Accordingly, in areas of fumarolic discharges, hot soils and anomalous diffuse soil degassing of incondensable gases, CO_2 flux can be used as a tracer of the whole process allowing to estimate the total amount of steam and thermal energy involved in the process.

Figure 4. Maps of soil temperature for the different hydrothermal sites (map coordinates are expressed, in m UTM-WGS84 19S).

4.3 The hydrothermal system feeding soil diffuse degassing and structural control on DDS

The main fumarolic emissions located in the five surveyed zones (Figs. 1 - 4) were sampled and analyzed in 2012. The concentration of main and relevant gas species, C and He isotopes and the temperature estimations calculated by gas geothermometry are reported in Table 1. H_2O is by far the main component, being > 97% by volume in all the fumaroles. The second component is CO_2, followed by minor amount of N_2, H_2, CH_4 and H_2S. CO and He concentrations are <1 ppm by volume. The absence of the strong acidic gases (i.e. SO_2, HCl and HF), which are typical of high temperature fumaroles from active volcanic systems, and the relatively high CH_4 contents suggest that these gases are intimately related to a hydrothermal system. According to Agusto et al. (2013), the fumarolic fluids are originated by boiling of a hydrothermal reservoir, mainly fed by meteoric water. However, the high $^3He/^4He$ ratios (R/Ra up to 7.04), the $\delta^{13}C$-CO_2 values of ~ -7‰ and the N_2/Ar ratios much higher than those of ASW (Air Saturated Water), suggest that He, N_2 and CO_2 are mainly supplied to the hydrothermal system by a magmatic source (Agusto et al. 2013; Tassi et al. 2015). Three deep wells, drilled in the eighties in the frame of a geothermal project (COP-1, COP-2 and COP-3 in Fig. 5; Dellapé and Pando 1975; Jurío 1977; Panarello et al. 1988; JICA-EPEN 1992; Sierra et al. 1992; Mas et al. 2000), provided direct information on the hydrothermal system feeding the CCVC diffuse degassing structures. All the 3 wells, which are located 1-2 km S or W of the studied hydrothermal sites (Fig. 5), reached a deep reservoir of high temperatures (240-260 °C) and a shallower vapor dominated zone at depths of 800-1,000 m for which temperatures from 200 to 215 °C were measured and/or estimated with geochemical indicators (Sierra et al. 1990; Panarello 2002).

Figure 5. Structural setting for area compared with the location of DDSs and geothermal wells. The area where we infer the presence at depth of a single phase vapor zone is highlighted.

Geothermometric calculations in the H_2O-CO_2-CH_4-CO-H_2 gas system (Tassi et al. 2015) indicated that the fumarolic fluids discharged at Piedra Copahue, Las Máquinas and Las Maquinitas equilibrate in a single vapor phase, as actually observed by the geothermal wells, at a temperature of 203-210 °C ($T_{H\text{-}C\text{-}O}$ in Table 1). Other computations, based on the CO/CO_2 ratios by applying the same method described in Chiodini et al. (2015), produced similar temperatures ($T_{CO\text{-}CO2}$ ~204-206 °C; Table 1). These estimations are in good agreement with the temperatures measured in the geothermal wells, suggesting the occurrence of a large, probably unique, vapor zone reached by the wells and feeding the hydrothermal manifestations of Termas de Copahue, Las Máquinas and Las Maquinitas ("hot area with evidences of a single phase vapor zone at depth" in Fig. 5). This would explain the remarkable chemical and isotopic homogeneity of the fumaroles from the 3 different sites (Table 1), which are distant a few kilometers from each other (Fig. 5). The three fumaroles show, for example, a similar H_2O/CO_2 molar ratio of ~40 and $^3He/^4He$ of ~7 R/Ra.

In order to better understand the role of this vapor zone in the hydrothermal circulation, the structural setting of the zone needs to be considered. The caldera is locally characterized by three fault systems, which are NE-SW, WNW-ESE and NW-SE oriented (Melnick et al. 2006; Rojas Vera et al. 2010; Latinoconsult 1981; JICA – EPEN 1992). These three fault systems are arranged in such a way that they constitute the borders of a triangle-shaped horst structure which, according to gravity and electrical resistivity surveys, represents a high conductivity zone of hot fluids circulation (JICA – EPEN 1992). The geometries of the DDS's, as defined by the ϕCO_2 distribution, are roughly consistent with these three directions (Fig. 5). In particular at Termas de Copahue, Las Maquinitas I and II the high CO_2 fluxes seem to be mainly distributed along the NE-SW-aligned structures, which correspond to either known faults or faults inferred by this investigation on the basis of diffuse degassing processes active in this area. At Las Máquinas, the DDS develops along both NE-SW and WNW-ESE structural trends. The general correspondence between the structural trends and the DDSs geometries suggests that the emission of the hydrothermal fluids is favored by the fault systems, which cut through the vapor zone, causing the transfer of the deep fluids towards the surface. In Figure 5, the extension of such vapor zone was roughly delimited: the studied DDS would be located in the northern and eastern limits of this "hot area" with the exception of Anfiteatro which, according to this hypothesis, would be positioned externally with respect to the "hot area". This is supported by the chemical and isotopic composition of the fumarolic fluids discharged at Anfiteatro, as they significantly differ from the other areas. The Anfiteatro fumaroles are indeed richer in water (H_2O/CO_2 molar ratio of ~100) and the $^3He/^4He$ ratio is significantly lower (R/Ra ~4.9) than those measured at Las Máquinas, Las Maquinitas and Piedra Copahue.

4.4 Estimation of the thermal energy release

At the Copahue hydrothermal sites, the thermal energy release was estimated by using an approach similar to that described in Chiodini et al. (2001; 2005). The computation was based on (i) the estimation of the pristine H_2O/CO_2 ratio ($R_{H2O-CO2}$ by weight) of the fluid feeding the soil diffuse gas emission before steam condensation and (ii) the computation of the total steam involved in the process Q_{steam} by multiplying $Q_{CO2,d}$ by $R_{H2O-CO2}$. In the case of Las Maquinitas, the measured fumarolic CO_2 flux (3.2 t d^{-1}) was added to the diffuse CO_2 output. In each hydrothermal site, Q_{steam} was computed with the reasonable assumption that $R_{H2O-CO2}$ is equal to the H_2O/CO_2 ratio measured in the fumaroles of the correspondent degassing structure (Table 5). The total amount of steam from each area (Q_{steam}) varies from 285 t d^{-1} at La Maquinitas to 1,506 t d^{-1} at Termas de Copahue (Table 5). The total thermal release QH_{tot} (Table 5) was calculated by adding three contributions:

1) QH_{res} represents the heat released by the H_2O-CO_2 gas mixture moving from the reservoir conditions to the condensation zone. The reservoir temperatures were considered equal to 210 °C, whilst the reservoir pressure was assumed that of the saturated vapor at which P_{CO2}, computed by multiplying P_{H2O} by the measured fumarolic CO_2/H_2O molar ratio, was added. QH_{res} was calculated by multiplying Q_{steam}

by the enthalpy difference between the vapor at reservoir conditions and at condensation conditions (0.096 Mpa and 98 °C). The computation was performed using MUFITS software, which allows to predict CO_2-H_2O mixture properties in a wide range of pressures and temperatures (Afanasyev, 2013). QH_{res} ranges from 0.5 MW to 3.6 MW, thus it is the minor term of the energetic balance of the diffuse degassing structures (Table 5);

2) QH_{cond} corresponds to the heat released during steam condensation at subsurface conditions. The QH_{cond} values, which were computed by multiplying Q_{steam} by the latent heat of condensation at 98 °C (2,262 J g^{-1}), range from 7.5 MW at Las Maquinitas I and II areas to 39.4 MW at Termas de Copahue (Table 5). QH_{cond} is the main term of the energy budget;

3) $QH_{cooling}$ is the heat released as the condensates cool down to ambient temperature. It was estimated by multiplying Q_{steam} by the enthalpy difference between the liquid at 98 °C (enthalpy = 411 j g^{-1}) and at 10 °C (enthalpy = 42 j g^{-1}). The $QH_{cooling}$ values, from 1.2 to 6.4 MW, were intermediate between those of QH_{res} and QH_{cond} (Table 5).

The total thermal energy release from the five-surveyed zones is 107.5 MW. The highest thermal energy release (49.1 MW) was estimated at Termas de Copahue, where the computed Q_{steam} was 1,506 t/d. Here, the production of large amount of condensates is shown by the mass balance calculated for the small creek (Rio Frio, Fig. 1) that enters the village with a flow rate of 560 t d^{-1} (pH = 6.06, T = 16.2 °C), collects the great majority of the condensation waters and flows out at the rate of 1,460 t d^{-1} (pH = 3.4, T = 22.5 °C). The measured flow rate increment, which is about 60% of the estimated condensate production in the area, appears to be realistically supporting the reliability of our estimation. It is indeed reasonable that part of the condensates is feeding the local aquifer (groundwater circulation).

Table 5. Heat flux estimation.

6. Conclusions

The north-western sector of the Caviahue caldera is characterized by fumarolic emissions associated with zones of anomalously high soil CO_2 diffuse degassing and soil temperature. Five of these sites were investigated and a total discharge of deeply-originated

CO_2 of ~165 t d^{-1} from soil diffuse degassing processes was estimated. The gas source for Termas de Copahue, Las Máquinas, Las Maquinitas I and II is a 800-1,000 m deep vapor zone with a temperature of ~200-215 °C, as indicated by both the data of three deep wells drilled in the eighties SW of the natural degassing sites, and gas geothermometry. The occurrence of a unique gas zone feeding the manifestations of the area explains the remarkable compositional homogeneity of the fumaroles, with the exception of those discharging at Anfiteatro, where significant compositional and isotopic differences with respect to the other sites were observed. Using CO_2 as a tracer of the original vapor phase, a natural thermal release of ~77 MW from Termas de Copahue, Las Máquinas, Las Maquinitas I and II was computed, and increases up to ~107 MW when the Anfiteatro degassing zone is considered.

The clear magmatic signature of the incondensable fumarolic gases, the wide expanse of the hydrothermal zones and the remarkable amount of gas and heat released by fluid expulsion, appear to be compatible with an active magmatic intrusion in the subsurface of this portion of the Caviahue caldera. This model well agrees with the proved occurrence of volcanic seismic tremor associated with the hydrothermal systems of the Copahue-Caviahue Volcanic Complex (Ibañez et al. 2008; Forte et al. 2012).

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Table 1. Chemical composition of the fumaroles of the surveyed areas (March 2012). Gas concentrations are expressed in µmol/mol, helium isotopes as R/Ra ($^3He/^4He_{sample}/^3He/^4He_{air}$). Equilibrium temperatures were calculated within the H_2O-H_2-CO_2-CO-CH_4 gas system (T_{H-C-O}; Tassi et al., 2015) and the geothermometer based on the CO/CO_2 ratio (T_{CO-CO2}; Chiodini et al., 2015).

Name	T °C	H_2O	CO_2	H_2S	N_2	CH_4	H_2	He	CO	R/Ra	T_{H-C-O} °C	T_{CO-CO2} °C
Las Máquinas	96	973000	25200	189	511	540	395	0.32	0.057	7.04	203	206
Las Maquinitas I	130	976000	23100	214	521	290	312	0.32	0.049	6.97	210	204
Termas de Copahue	95	975000	24100	212	449	286	319	0.30	0.052	7.01	210	204
Anfiteatro	92	989000	9470	213	4045	641	184	0.24	0.068	4.93	258	244

Table 2. Main parameters of the five surveyed areas.

Name	Extension (m^2)	No. of points	Mean (min-max) ϕCO_2 ($g\ m^{-2}\ d^{-1}$)
Las Máquinas	320,823	495	145 (<0.05 – 7,270)
Las Maquinitas I	45,842	141	78 (<0.05 – 2,200)
Las Maquinitas II	32,802	103	272 (<0.05 – 14,330)
Anfiteatro	26,089	346	105 (<0.05 – 16,560)
Termas de Copahue	575,748	678	195 (<0.05 – 9,380)
Total	1,212,585	1763	158 (<0.05 – 16,560)

Table 3. Estimated parameters and partitioned populations in the 5 surveyed areas.

Name	Population	Proportion (%)	Average ϕCO_2 and 90% confidence interval ($g\ m^{-2}\ d^{-1}$)	Total diffuse CO_2 output and 90% confidence interval ($t\ d^{-1}$)
Las Máquinas	A (background)	8	1.01 (0.82 - 1.23)	0.03 (0.02 - 0.03)
	B (background)	78	24 (22 - 27)	5.9 (5.3 - 6.6)
	C (endogenous)	12	388 (276 - 538)	15 (11 - 21)
	D (endogenous)	2	4,379 (3,058 – 6,038)	28 (20 - 39)
	Total	100		49 (36 - 66)
Las Maquinitas I	A (endogenous)	100	95 (49 - 181)	4.4 (2.2 - 8.3)
La Maquinitas II	A (background)	55	4.9 (4 - 6)	0.09 (0.07 - .11)
	B (endogenous)	37	86 (56 - 128)	1 (0.7 - 1.6)
	C (endogenous)	8	5,815 (1,298 – 1,5995)	15.3 (3.4 - 42)
	Total	100		16 (4 - 44)
Anfiteatro	A (background)	12.5	<0.1	nd
	B (background)	40.5	6.7 (5.2 - 8.7)	0.64 (0.49 - 0.83)
	C (background)	44	26 (21 - 32)	2.7 (2.2 - 3.3)
	D (endogenous)	3	5,634 (1,213 – 15,022)	40 (9 - 106)
	Total	100		43 (11 - 110)
Termas de Copahue	A (background)	8	0.99 (0.89 - 1.10)	0.05 (0.04 - 0.05)
	B (background)	73	22 (19 - 25)	9.2 (8.1 - 10.4)
	C (endogenous)	19	1,000 (784 – 1,270)	109 (86 - 139)
	Total	100		119 (94 - 174)

Table 4. Relevant parameters of SGS application and estimation of the total CO_2 output from Copahue hydrothermal sites.

Site name	Variogram model, nugget, range (m)	Grid parameters: n.cells, lag (m)	Total CO_2 release ± standard deviation (t d-1)	Endogenous CO_2 release, Q_{CO2} (t d-1)
Las Máquinas	Spherical, 0.47, 145	35647, 3	42.7 ± 4.33	36.8
Las Maquinitas I	Spherical, 0.51, 50	45842, 1	5.01 ± 0.81	5.0(1)
Las Maquinitas II	Spherical, 0.46, 66	32802, 1	8.30 ± 1.56	8.3
Anfiteatro	Spherical, 0.71, 80	29748, 3	24.0 ± 2.45	21.7
Termas de Copahue	Spherical, 0.59, 194	63972, 3	100 ± 5.42	90.8
Total	-	-	180	162.6

(1) At Las Maquinitas I, an additional CO_2 flux of ~ 3.2 t d-1 was measured from the main fumarolic vent.

Table 5. Heat flux estimation.

Hydrothermal site	$\mathbf{R_{H2O\text{-}CO2}}$	$\mathbf{Q_{steam}}$ **(t d^{-1})**	$\mathbf{QH_{res}}$ **(MW)**	$\mathbf{QH_{cond}}$ **(MW)**	$\mathbf{QH_{cooling}}$ **(MW)**	$\mathbf{QH_{tot}}$ **(MW)**
Las Máquinas	15.8	581	1.2	15.2	2.5	18.9
Las Maquinitas I, II [(1)]	17.3	285	0.5	7.5	1.2	9.1
Termas de Copahue	16.6	1506	3.2	39.4	6.4	49.1
Anfiteatro	42.7	927	2.2	24.3	4.0	30.4
Total	**-**	**3244**				**107.5**

[(1)] At Las Maquinitas Q_{steam} includes the contribution of the main fumarolic vent which was computed in 55 t d^{-1} by multiplying the measured CO_2 flux (3.2 t d^{-1}) by $R_{H2O\text{-}CO2}$.

Figure
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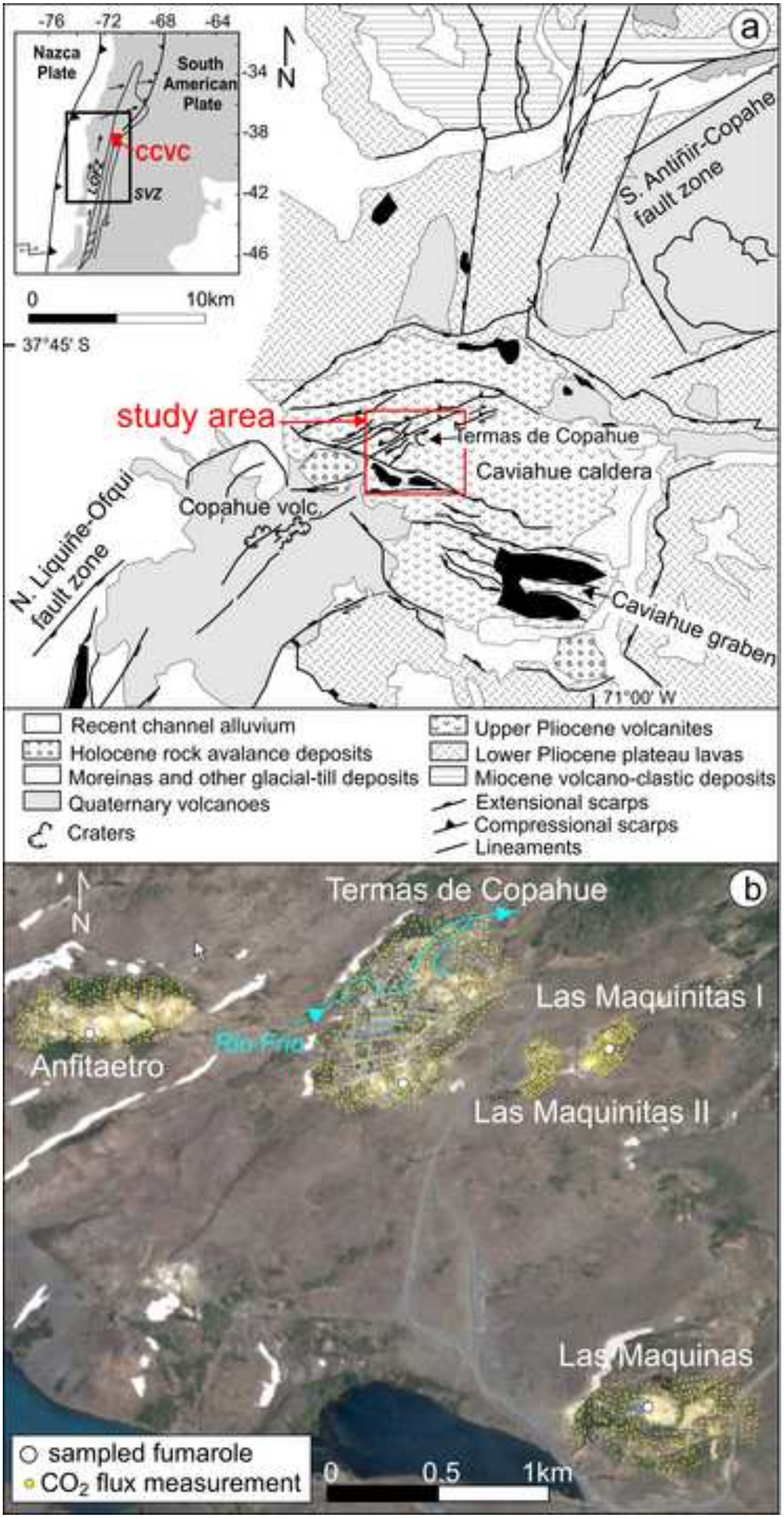

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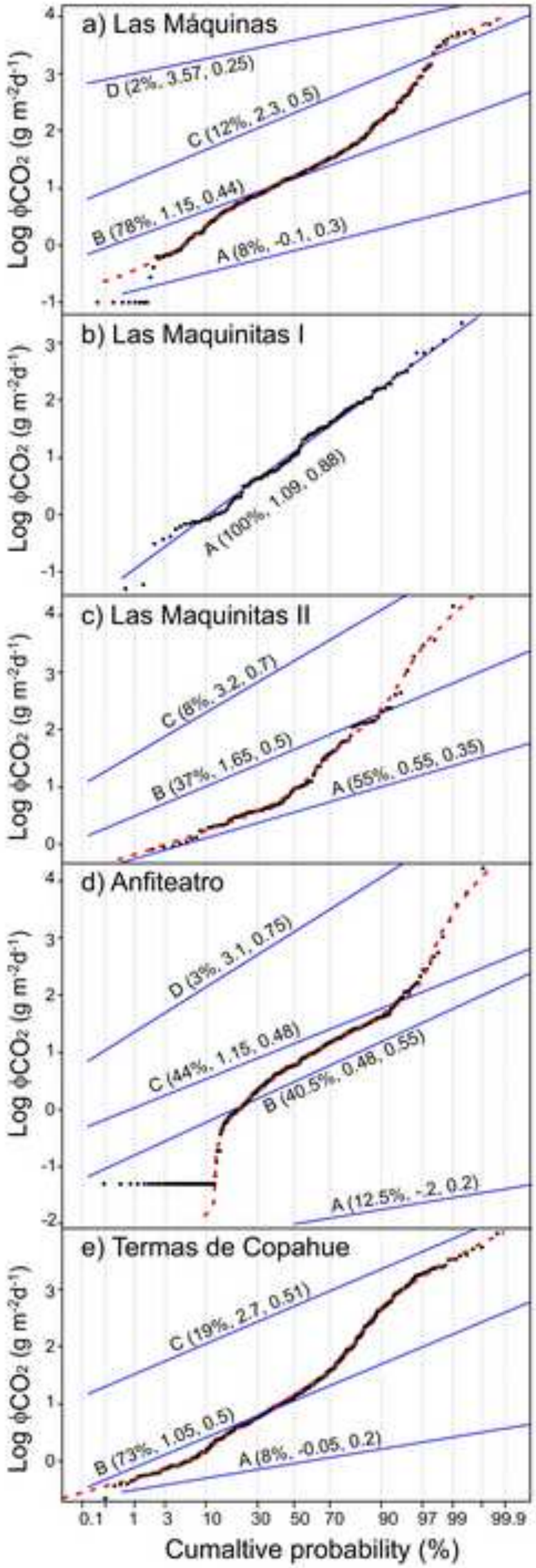
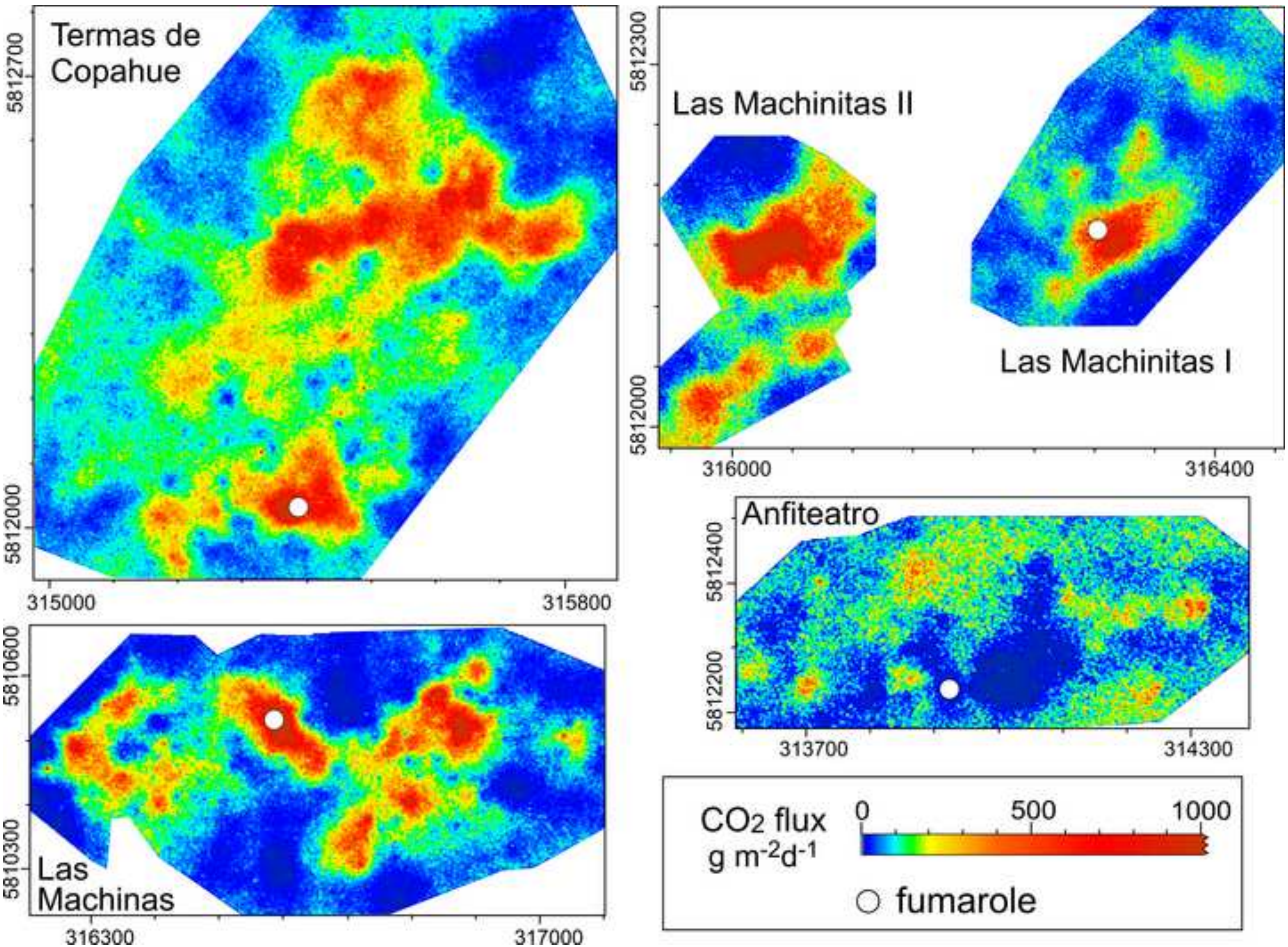


Figure


Termas de Copahue
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5812000
315000
315800
Las Machinitas II
Las Machinitas I
5812300
5812000
316000
316400
Anfiteatro
5812400
5812200
313700
314300
Las Machinas
5810600
5810300
316300
317000
CO2 flux g m-2d-1
0
500
1000
fumarole

Figure

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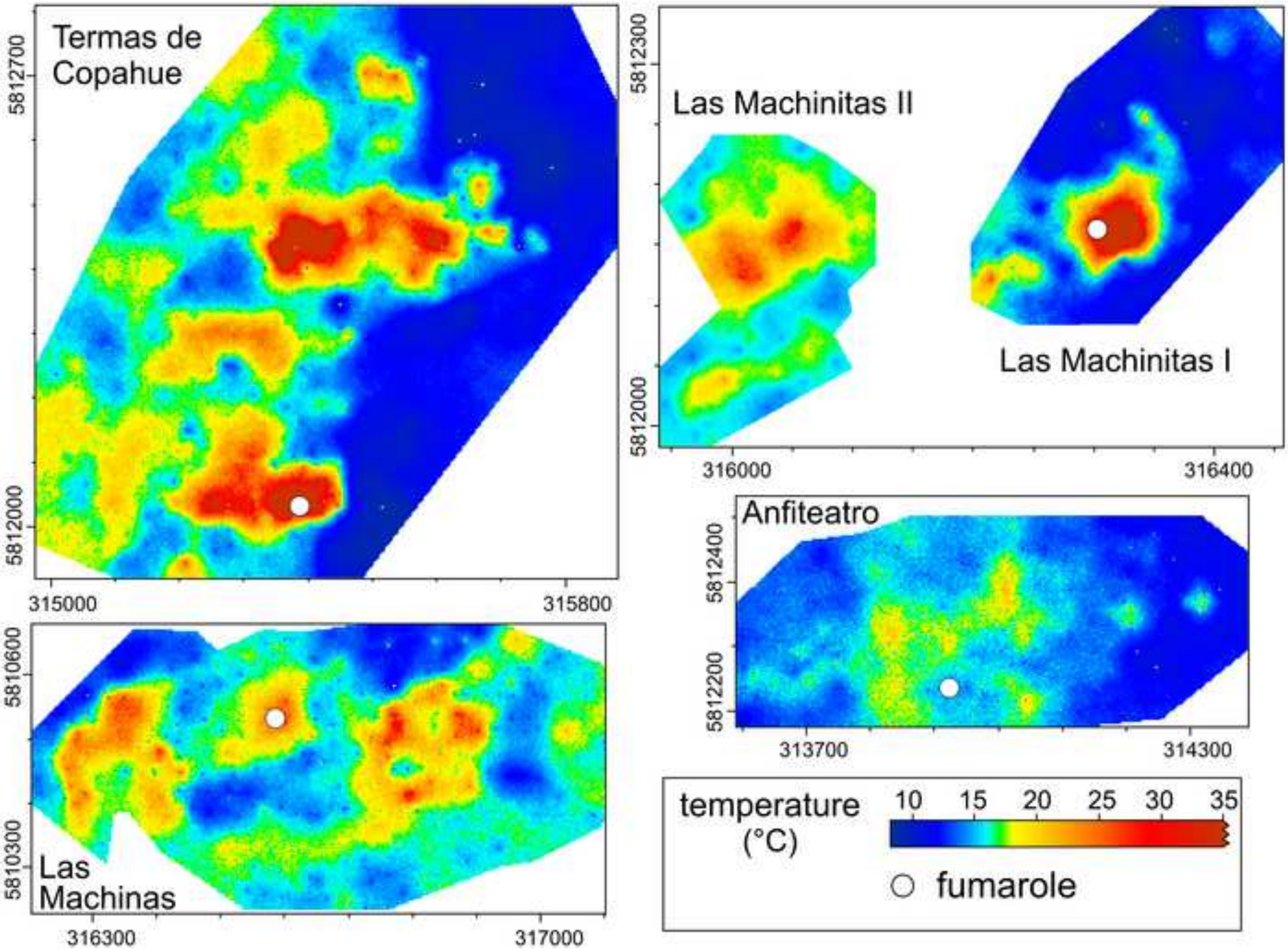

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