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Distribution and origin of soil gas CO_2 and CH_4 in and around Cañadas caldera, Tenerife, Canary Islands, Spain

Distribución y origen de los gases CO_2 y CH_4 en los suelos de las Cañadas y alrededores, Tenerife, Islas Canarias

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ABSTRACT

The distribution and origin of soil gas CO_2 and CH_4 were investigated to have a better understanding on the levels of diffuse degassing at the surface enviroment of Cañadas caldera (Tenerife, Canary Islands). Soil gas CO_2 and CH_4 distribution analysis showed a quite clear relationship with volcanic and geothermal features on the study area. Carbon isotope measurements showed a magmatic, mixed magmatic-biogenic, and biogenic origin for the soils gas CO_2 while a biogenic origin was mainly found for the soils gas CH_4 at Cañadas caldera and its surroundings.

RESUMEN

El origen y la distribución espacial de CO_2 y CH_4 en el horizonte edáfico de la caldera de las Cañadas se investigó para evaluar los niveles de desgasificación difusa en el ambiente superficial de esta estructura volcánica. La evaluación y el análisis de la distribución del CO_2 y CH_4 en los suelos indican una relación muy clara con las principales características volcanico-geotermales del área de estudio. Las medidas de isótopos de carbono indican un origen magmático, mixto magmático-biogénico y biogénico para el CO_2, mientras que un origen biogénico fue detectado principalmente para el CH_4 en los suelos de la caldera de las Cañadas.

Key words: *Soil gases, CO_2, CH_4, carbon isotopes, Cañadas Caldera, Canary Islands.*

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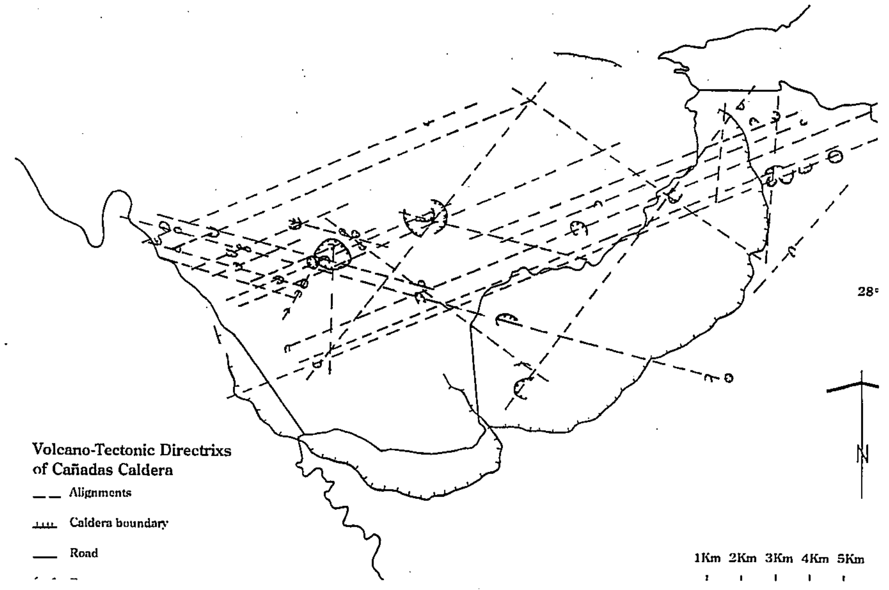

Fig. 1.- Map of volcanic-tectonic directrixs at Cañadas caldera.

Fig. 1.- Mapa de las directrices volcanico- tectónicas en la caldera de Las Cañadas

Introduction

Diffuse degassing from active volcanic centers is receiving more and more interest for both geothermal and volcanic surveillance studies. A continuos CO_2 emission of deep origin flushes most if not all geothermal systems (Mahon *et al.*, 1980). Soil gas CO_2 anomalies in geothermal surveys showed a good agreement with those defined by soil gas Hg°, total Hg, and ^{222}Rn in the Broadlands geothermal area, New Zeland (Koga *et al.*, 1982). Sheppard *et al.*, (1990) compared also soil gas Hg°, total Hg and soil gas CO_2 anomalies over three geothermal areas, with a variable agreement between these components.

High levels of CO_2 emission are released to the atmosphere from active volcanic areas not only during the eruptions but also during quiescent periods. These CO_2 discharges occur as plumes and fumaroles from active craters as well as diffuse degassing from the flanks of volcanic edifices (Baubron *et al.*, 1990; Allard *et al.*, 1991). Several other studies have examined CO_2 emissions through the surface environment over active volcanies (Aubert and Baubron, 1988: Badalamenti *et al.*, 1988; 1991; Giammanco *et al.*, 1995). On the contrary very few studies have been

Population	$\langle x \rangle \equiv 50\%$	$\langle x \rangle + \sigma \equiv 84\%$	$\langle x \rangle - \sigma \equiv 16\%$
I	820	1200	550
II	2900	4500	1900
III	9000	13800	5800
IV	110000	270000	56000

Table 1.- Statistical results for soil gas CO_2 distribution at Cañadas caldera.

Tabla 1.- Resultados estadísticos de la distribución CO_2 en la caldera de Las Cañadas.

reported about the origin, distribution and flux of CH_4 from active volcanic-geothermal areas.

The investigated area (Fig. 1) involves the Cañadas caldera and its surroundings.

This structure is crossed by an allineation of fractures and volcanic cones (Coello *et al.* 1981) and presents a obvious geothermal feature at the summit crater of Teide volcano (3718 m) (Fig. 1). The climate in this area, type subalpine, is characterized by strong climate contrasts at the different seasons. The annual rainy average is approximately 500 mm. The vegetation over 1900-2000 m changes from pine grove to endemic shrubs.

Sampling and analysis

Soil gas samples were collected at Cañadas Caldera and its surroundings after following carefully considerations of the local geology and structure. Soil gas collection was carried out by using 10 cc vacutainers and PVC pipes which were inserted at 40 cm depth and left in the ground for a 7 days period to reach soil atmosphere equillibration.

The soil gas CO_2 and CH_4 compositions were performed by using a TDC gas chromatograph. Approximately 350 and 150 soil gas samples were analyzed for soil CO_2 and CH_4, respectively. Carbon isotope measurements of soil CO_2 and CH_4 were carried out by a GC-IRMS in 36 samples. The carbon isotopic compositions of CO_2 and CH_4 were separately determined by conventional methods (Sakai *et al.*, 1976; Ono *et al.*, 1993). All measurements were carried out at the Laboratory for Earthquake Chemistry of The University of Tokyo.

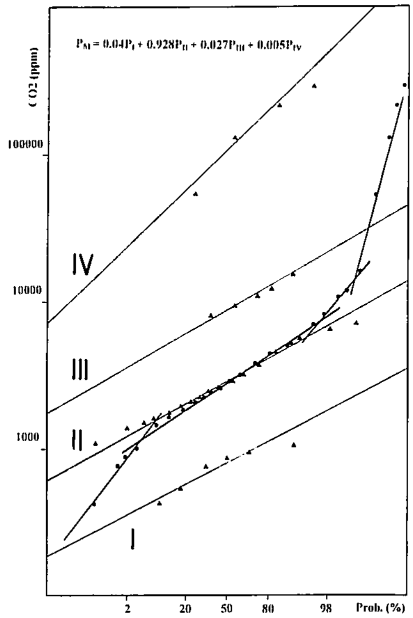

Fig. 2.- Accumulated frecuency diagram for soil gas CO_2 concentrations at Cañadas caldera.

Fig. 2.- Diagrama de frecuencias acumuladas de las concentraciones de CO_2 en la caldera de Las Cañadas.

Results and discussion

Sinclair statistical-graphical analysis (Sinclair, 1976) of soil gas CO_2 showed four overlapping geochemical populations (Fig. 2). The background (population II) mean is 2900 ppm and represents 92.8% of the total data. The peak group (population IV) showed a mean of 110,000 ppm CO_2 (11% CO_2) and represents 0.5% of the total data. An intermediate "threshold" population (population III) which represents a mixing between background and peak values had a mean of 9000 ppm CO_2 with a 2.7% of the total data. An additional intermediate population (population I) was observed and it is mainly related to atmospheric disturbance of soil CO_2 background levels (atmospheric CO_2 is approximately 380 ppm). Population I showed a mean of 820 ppm CO_2 and represents 4% of the total data (Table 1).

Statistical-graphical analysis for the 150 measurements of soil gas CH_4 indicated three overlapping populations (Fig 3): background (population II) and two intermediate populations (population I and III). The background had a mean of 195 ppm CH_4 and represents 63% of the total data. Population III represents a a mixing between CH_4 and background values and a peak population which was not detected, but it does not mean that it does not exist. This "threshold" population showed a mean of 410 ppm CH_4 and represents 16% of the total data (Table 2). Population I had a mean of 35 ppm CH_4 and might be related to atmospheric disturbances in the soil atmosphere. .

Chemical characterization of these gas samples show higher N_2/Ar molar ratios than atmospheric value (84) so implies that atmospheric contamination is negligible

Most of the caldera and its surroundings showed background levels of diffuse degassing of CO_2. Soil gas CO_2 levels at Cañadas caldera are relatively low with respect to other active calderas such as (1) Long Valley (USA), where significant amounts of soil gas CO_2 (up to 90%) of mantelic origin are responsible for killing trees (Farrar *et al.*, 1995), and (2) Rabaul (Papua New Guinea), where soil gas CO_2 measurements reach values up to 20% far away from active volcanic craters but just above high seismic areas (Pérez *et al.*, 1995). The different degree of volcanic activity might be a plausible explanation for these observed differences of soil gas CO_2 levels in these macro-scenarios. Most of the CO_2 released by the volcanic-hydrothermal system at Tenerife island might be also trapped in the relatively low temperature volcanic aquifer with shows mainly a high bicarbonate composition for the ground waters (Farrujia de la Rosa *et al.*, 1994).

A close relationship is suggested between high soil gas CO_2 distribution pattern and volcanic-geothermal features at Cañadas caldera. Anomalously high soil gas CO_2 values (>100x background, 30%) were identified with the most obvious geothermal and volcanic features at Cañadas caldera: Teide submit crater and tectonic-volcanic directrixs. This value is similar to soil gas CO_2 concentrations measured in the summit crater of Etna volcano (27.9% CO_2) (Allard *et al.*, 1991). High soil gas CO_2 concentrations were also identified at the NW area of Cañadas caldera where exist an intensive vegetation (pine grove) and where soil samples showed also low pH values (4<pH<5) (Fig. 4). These relatively high soil gas CO_2 values might be related to degradation of the organic matter, process enhanced by the acidity and permeability of these soils (Hernández *et al.*, 1994).

In the case of soil gas CH_4, most of the caldera and its surrounding also showed CH_4 background levels. The highest value of CH_4 (851 ppm) was detected outside Cañadas caldera where occurs relatively high temperature ground waters (T>30°C). This anomalously high CH_4 value is geographically also well correlated with the existence of horizontal drillings for ground water explotation (galeries) wich show high level of CH_4 in their inner atmosphere (Fig. 5). Ground waters from this area show high bicarbonate content; therefore, high soil gas CO_2 levels were not detected.

High soil gas CO_2 and CH_4 concentrations are well correlated with the anomalously high ^{222}Rn and Hg (total) values found at Cañadas caldera and its surroundings (Hernández P. A. *et al.*, 1993; 1994). This correlation ratify the existence of high heat flow zones in and around Cañadas caldera.

The carbon isotopic composition of CO_2 and CH_4 are listed in Table 3. Three differents groups of $\delta^{13}C$ values for soil gas CO_2 can be observed. Soil gas samples from the summit crater of Teide volcano showed the heaviest signature of carbon isotopic composition for soil gas CO_2. $\delta^{13}C(CO_2)$ in these samples showed a range from -8.3‰ to -12.9‰ relative to PDB. The soil gas sample with a $\delta^{13}C(CO_2)$ = -8.3‰ clearly suggests a magmatic origin for the soil gas CO_2, and a atmospheric origin must be neglected because of the high soil gas CO_2 concentration of this sample (296,423 ppm). This isotopic value is quite similar to the carbon isotopic composition of the gases discharged by the fumarolic system from Teide volcano which shows a range of $\delta^{13}C(CO_2)$ from -3.7‰ to -8.1‰ and high observed $^3He/^4He$ ratios, 7.5 Ra (Pérez *et al.*, 1994; 1996). On the contrary, the soil gas sample with a $\delta^{13}C(CO_2)$ = -12.9‰ might suggest a potential mixing between magmatic and biogenic soil gas CO_2 and atmospheric disturbance should be also neglected because of the observed high soil gas CO_2 concentration. The second group showed a $\delta^{13}C$ (CO_2) range from -12.9‰ to -18‰ relatively to PDB. This relatively heavier isotopic signatures for soil gas CO_2 might be also related to a mixing process between biogenic and magmatic CO_2 because of the relatively high CO_2 concentrations in these samples which are not only located in vegetated areas. The group which showed the most ligthest carbon isotopic signature for the soil gas CO_2 had a range of $\delta^{13}C(CO_2)$ from -18.8‰ and -38.0‰, and they are mainly biogenic in origin. In the case of soil gas CH_4, carbon isotope measurements suggested mainly a biogenic origin for the methane at Cañadas's surface environment.

Population	⟨x⟩ ≡50%	⟨x⟩ + σ ≡84%	⟨x⟩ - σ ≡ 16%
I	35	104	140
II	195	270	2.90
III	410	480	350

Table 2.- Statistical results for for soil gas CH_4 distribution at Cañadas caldera

Tabla 2.- Resultados estadísticos de la distribución CH_4 en la caldera de Las Cañadas.

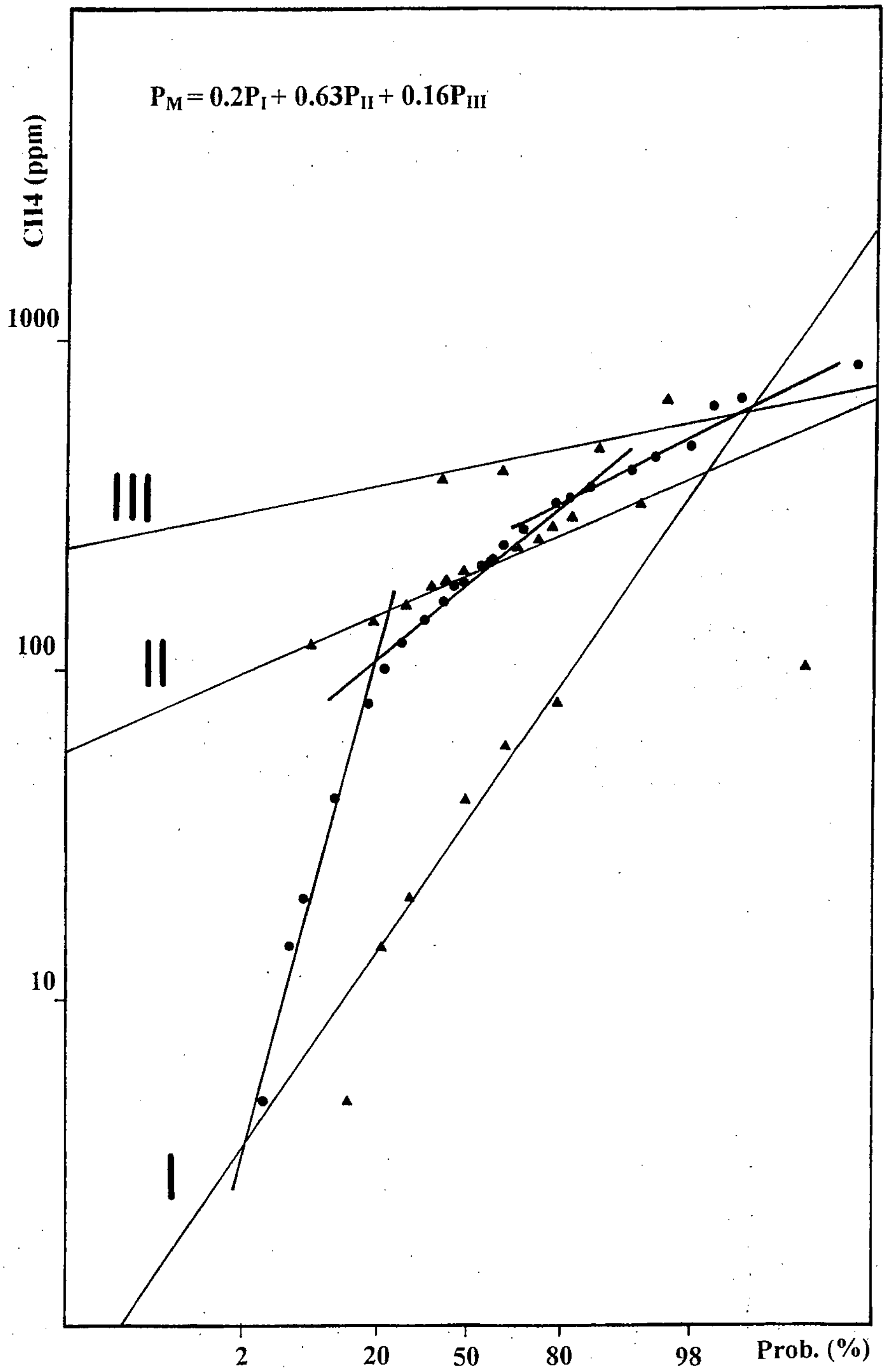

Fig.3.- Accumulated frecuency diagram for soil gas CH_4 concentrations at Cañadas caldera.

Fig. 3.- Diagrama de frecuencias acumuladas de las concentraciones de CH_4 en la caldera de Las Cañadas.

Conclusions

Soil gas CO_2 and CH_4 results showed four and three different geochemical populations which are mainly due to deep-

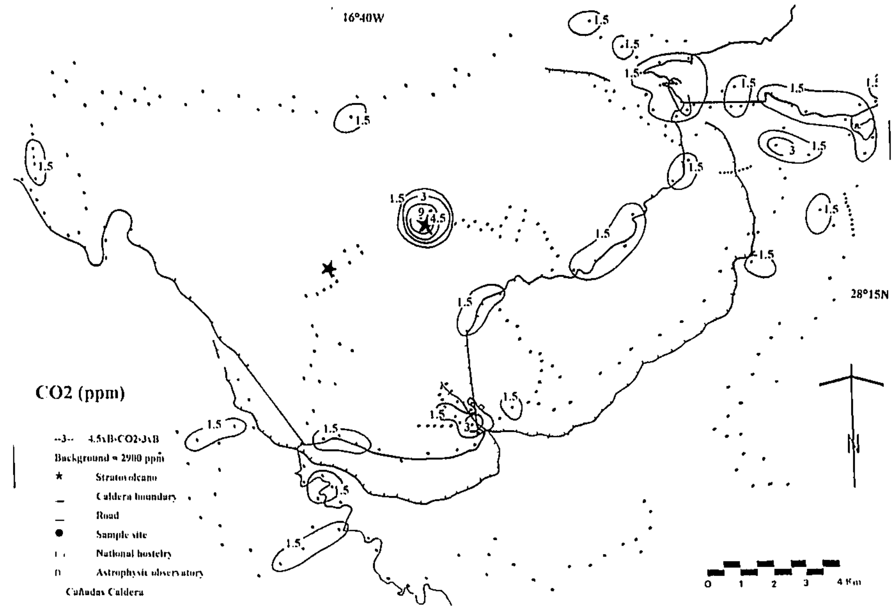

Fig. 4.- Soil gas CO_2 distribution at Cañadas caldera, Tenerife, Canary Islands.

Fig. 4.- Distribución de CO_2 en los suelos de la caldera de Las Cañadas,Tenerife, Islas Canarias.

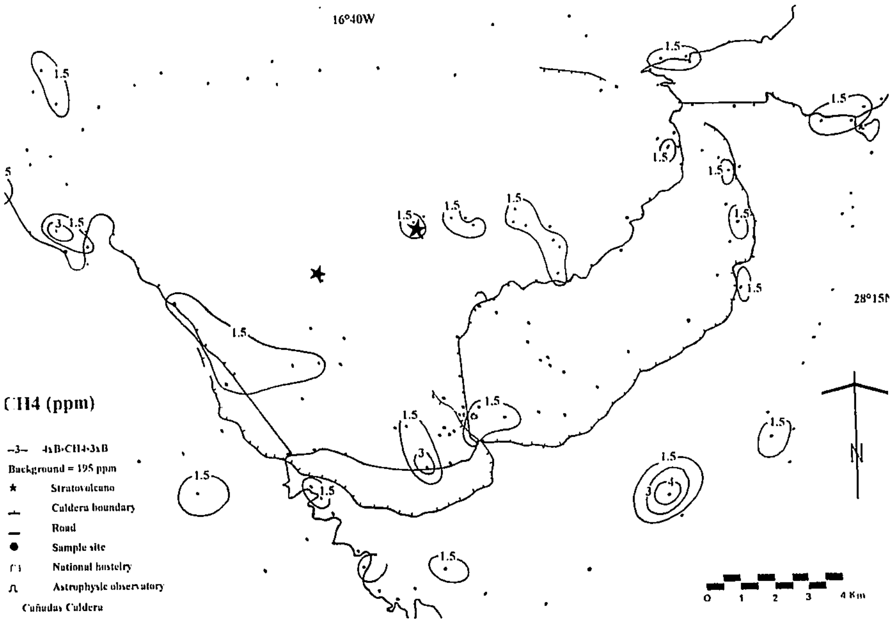

Fig. 5.- Soil gas CH_4 distribution at Cañadas caldera, Tenerife, Canary Islands.

Fig. 5.- Distribución de CH_4 en los suelos de la caldera de Las Cañadas,Tenerife, Islas Canarias

seated and atmospheric disturbances on the surface environments at Cañadas caldera. The distribution pattern of soil gas CO_2 and CH_4 showed a clear agreement with volcanic and geothermal features of Cañadas caldera. high soil gas CO_2 and CH_4 levels reveal mainly deep perturbations or clear magmatic origin in the case of soil gas CO_2. Further investigations will focuss on soil gas CO_2 and CH_4 fluxes from Cañadas caldera.

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