Anomalous soil gas CO_2 concentrations and relation to seismic activity at Rabaul caldera, Papua New Guinea

Niveles de concentración anomalos de CO_2 en los suelos y su relación con la actividad sísmica de la caldera de Rabaúl, Papua Nueva Guinea

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Resumen

Medidas de CO_2 en los suelos de la caldera de Rabaul, Papua Nueva Guinea, reflejan niveles de concentración altos, hasta cerca de un 20%, en relación con un margen activo de la caldera definido por sismicidad. Estos niveles anómalos del CO_2 en los suelos fueron detectados lejos de los aparatos volcánicos activos. La caracterización isotópica de carbono refleja un origen principalmente biogénico para el CO_2, pero aquellas muestras que presentan un mayor contenido de CO_2 muestran una firma isotópica relativamente más pesada.

Key words: *Soil gas CO_2, C isotopes, Seismicity, Rabaul, Papua New Guinea*

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Introduction

Significant amounts of CO_2 are released to the atmosphere from active volcanic areas not only during eruptive stages but also during quiescent periods. This CO_2 emission from volcanic areas does not only occur from plumes and fumaroles, but also as diffuse outgassing from the surface environment (Aubert and Baubron, 1988; Allard *et al.*, 1991; Baubron *et al.*, 1990, Farrar *et al.*, 1995). Diffuse degassing monitoring in active volcanic systems is becoming an important tool for seismic-volcanic prediction studies because it can be carried out far away from active craters where volcanologists might experience a high level of risk. Changes in gas and volatile concentrations in the soils in volcanic areas have been used to detect changes in fluid flow resulting from seismic activity and magmatic intrusion (Varekamp and Buseck, 1984, Williams, 1985; Badalamenti *et al.*, 1988; Giammanco *et al.*, 1995; Farrar *et al.*, 1995). These observations can be a very important issue for volcanic scenarios such as caldera and rift zones where an eruption might build up new volcanic vents. In previous studies, the analysis and evaluation of soil gas and volatile distribution patterns have been quite useful to detect areas of high heat flow which can become potential sites for new volcanic vents in active calderas (Williams, 1985; Pérez and Williams, 1990; Pérez, 1992; Salazar *et al.*, 1995). The aim of this study is to evaluate the existence of gas-flow through the seismic annulus structure defined during the unrest period of Rabaul caldera (Mori and McKee, 1987) by means of soil gas CO_2 measurements along a transect.

Sampling and analytical procedures

Soil gas samples were collected by using PVC pipes which were inserted in the ground at 40 cm. depth on November 1995. The upper part of the PVC pipes were closed by a cap with a septum to allow soil gas collection by using a syringe, while the lower part were open to allow soil gas to enter inside the PVC containers. Soil gas samples were collected after 5 days to allow soil gas atmosphere equilibration inside the PVC pipes.

A soil gas transect (A-A') of 43 sampling sites was carried out from the south of Matupit Island to the Northern part of the caldera between November 21-27, 1995(Fig.1) following a selected space-sampling according to geological and geophysical characteristics of the area. This geochemical profile was designed to intersect the seismic annulus defined by the 1980s seismic-uplift crisis at Rabaul caldera (Mori and McKee, 1987) and to be far away from the active volcanic vents to avoid interferences of degassing from volcanic vents. Soil gas samples were transferred to 10 cc. pre-evacuated vacutainers and CO_2 measurements were carried out by Gas Chromatograph. Selected soil gas samples were also analyzed for their isotopic composition of carbon in both soil CO_2 and CH_4 by a GC-IRMS in the Laboratory for Earthquake Chemistry at the University of Tokyo.

Results and discussion

Forty soil gas samples were collected along the N-S trending transect on November 27, 1995, and analyzed for soil gas CO_2 concentrations and carbon isotopic composition of soil gas CO_2 and CH_4 during the first week of December, 1995. Soil gas CO_2 concentrations varied widely from 1045 ppm CO_2 (0.1% CO_2) to 196335 ppm CO_2 (19.6% CO_2). Spatial variations of soil gas CO_2 concentrations along the transect are shown in Figure 2, soil gas CO_2 levels peaked (up to 19.63%) along the seismically active fault zone (Mori and

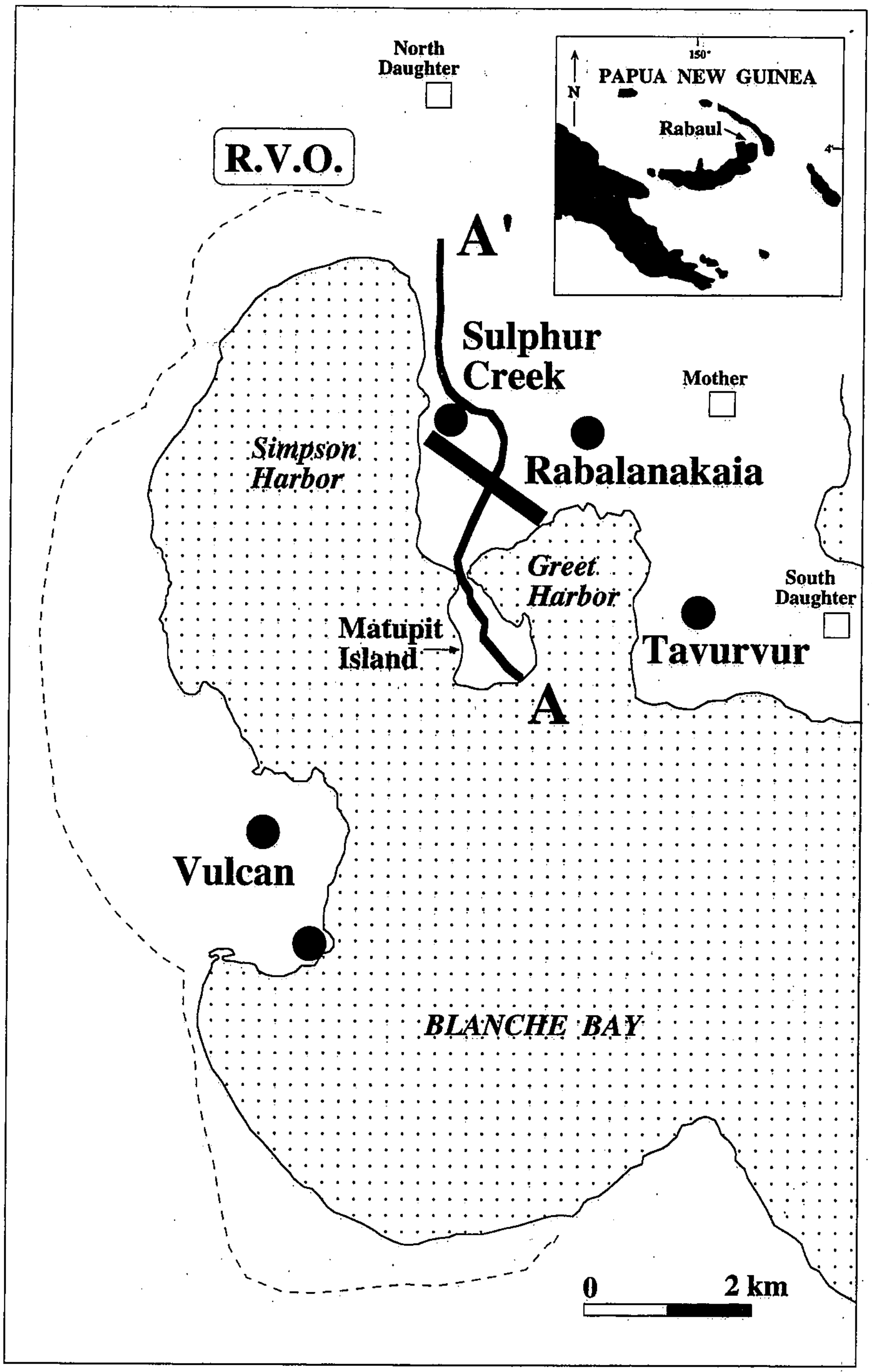

Fig.1 Rabaul caldera map and detail of soil CO_2 transect. Volcanic centers post-caldera (solid circles) and pre-caldera (empty rectangles). RVO, location of the Rabaul Volcano Observatory. Caldera's topographic limits (dashed line) and old airport (dark rectangle).

McKee, 1987), near the old airport, at some distance from both Tavurvur and Vulcan which did erupt simultaneously on September 1994 (McKee *et al.*, 1994). These anomalously high levels of soil CO_2 are lower than those observed on the flank of Mammoth Mountain where soil gas CO_2 concentrations exceeded 30% (> 90% at several locations) and is being responsible for the killing of trees in the area (Farrar *et al.*, 1995). One significant difference between these two scenarios is that soil gas CO_2 measurements at Rabaul were designed to be relatively far away from active volcanic centers in the caldera while soil gas CO_2 survey at Long Valley was performed to evaluate diffuse «flank» emissions of magmatic CO_2 near by Mammoth Mountain, a large dacitic volcano. In the case of Rabaul caldera, seismic activity related to the unrest of this volcanic structure since the 1970s have clearly defined a seismic annulus which represents the actual caldera boundaries. Airport's area, near the old airfield, is the only subaerial location where soil gas surveys can intersect this seismic structure to evaluate diffuse gas-flow through this seismological-defined fault and without being affected for significant levels of degassing from active volcanic centers in the caldera. After evaluating all these observations, we might suggest that relatively high observed soil gas CO_2 concentrations at Airport represent a good geochemical indicator of gas-flow along this structure which can be defined as an active fault by geophysical and geochemical observations. Previous studies of soil gases at Rabaul caldera revealed relatively high ^{222}Rn levels (>6 x B and >9 x B, where B= background = 1.57 pCi/l) and relatively low Hg^0 (<7.7 ppb, Background= 23.0 ppb of Hg^0) where the highest soil gas CO_2 were observed in the 1995 survey. This coupled observation of relatively high ^{222}Rn and low Hg^0 had been interpreted in other studies as active flush zones where a combination of mass and heat transport can account for this soil gas signature (Williams, 1985; Pérez, 1992). High soil gas CO_2 concentrations at Airport area could be also related to the effects of a higher thermal gradient along this active fault zone which might be also responsible for the potential release of Hg^0 from the surface environment..

Other anomalously high soil gas CO_2 concentrations were seen at the Matupit causeway where an additional fault has been defined by geochemical (anomalous soil gas ^{222}Rn and Hg^0) and geophysical methods (Pérez, 1992; McKee, personal communication) and near by Sulphur Creek area. Relatively low concentrations were observed at others sections of the transect, but the lowest values were detected at Matupit Island where a maximum uplift was observed in relation to the 1983-85 seismic-volcanic crisis at Rabaul caldera (McKee *et al.*, 1985). These low soil gas CO_2 concentrations observed at Matupit agree quite well with the observed high soil pH values (> 8.01) in the area (Pérez and Williams, 1991, Pérez, 1992). Soil pH measurements related to other areas of this transect showed background levels (6.01< pH< 8.00).

Carbon isotopic analysis of soil gas CO_2 and CH_4 in six selected samples (Fig.2) are listed in Table 1. $\delta^{13}C$ values of CO_2 ranged from -29.8‰ to -18.4‰

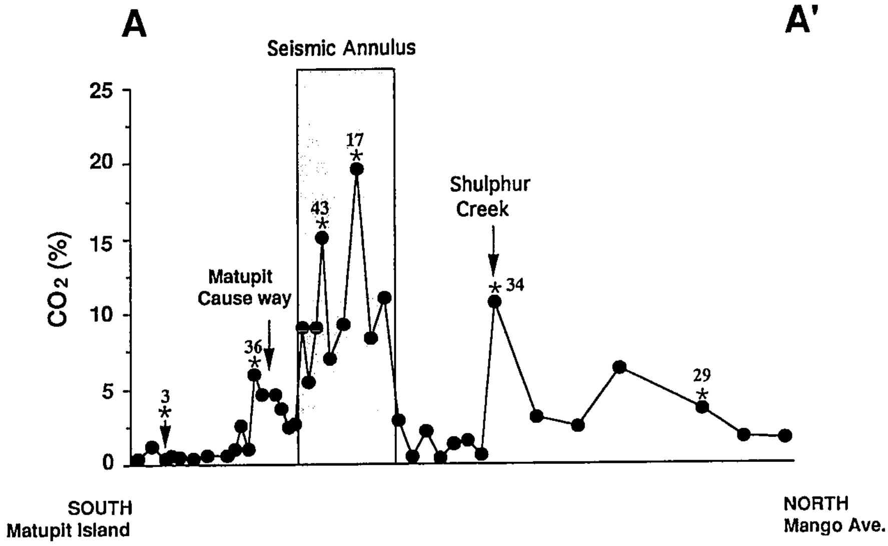

Fig.2 Soil gas CO_2 transect at Rabaul caldera along transect A-A'. Soil gas samples selected for carbon isotope measuerements are indicated.

Fig. 2.-Transecto de CO_2 en lossuelos de la caldera de Rabaúl siguiendo un perfil A-A'. Las muestras de gases en suelos analizados para isótopos de carbono son indicados

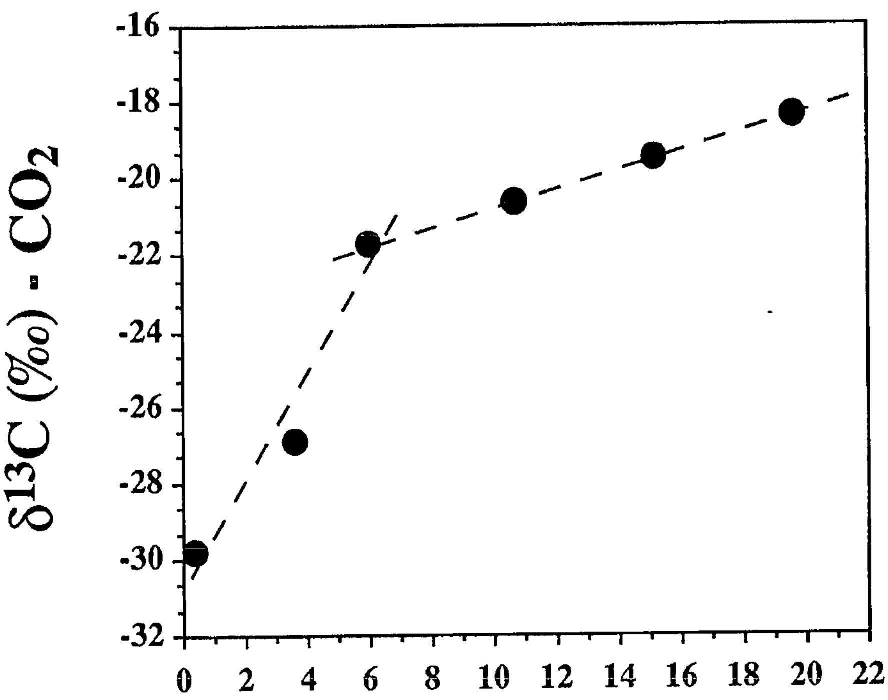

Fig.3 Relationship between soil gas CO_2 concentrations and $d^{13}C$-CO_2 from Rabaul caldera. Dashed lines represent two different trends.

Fig. 3.- Relación entre la concentración de CO_2 en los suelos $d^{13}C$-CO^2 enla caldera de Rabaul. Las lineas discontinuas representan dos tendencias diferentes

suggesting mainly a biogenic origin for the CO_2. The relationship between soil gas CO_2 concentrations and carbon isotopic signature of the CO_2 for these six samples reflects a very interesting pattern (Fig.3). An increase of soil gas CO_2 is accompanied by an increase in the $\delta^{13}C$ values. This trend showed a good linear regression with a correlation coefficient of 0.83, but this diagram suggest also that the data's distribution might follow two different regression lines (dashed lines in the Fig.3). After selecting the four samples with heavier isotopic signature, diagram of Abiogenic CO_2 vs $\delta^{13}C$ was constructed (Fig.4). All the data fit quite well according to the following linear regression equation

$$\delta^{13}C\,(‰)\text{-}CO2 = -23.176 + 0.24288\,[CO_2]\,(1)$$

which show a correlation coefficient of 1.00. Assuming that $\delta^{13}C$ values for magmatic CO_2 is around - 5.0 (‰), we can estimate what levels of soil gas CO_2 would be expected to be related to a significant diffuse magmatic degassing. This assumption might be reasonable because volcanic-hydrothermal discharges from Tavurvur volcano showed a carbon isotopic signature of -5.1‰ for the CO_2. Following this equation, soil gas CO_2 concentrations around 75% can be linked to a clear magmatic origin. These estimates are in good agreement with soil gas CO_2 data from Long Valley where clear magmatic signatures of CO_2 were observed in soil gas samples with abiogenic CO_2 concentrations > 80% . On the contrary, soil gases collected inside of active craters withCO_2 concentrations around 30% showed already a clear magmatic signature (Allard *et al.*, 1991, Hernández *et al.*, 1996). These main differences are mainly related to the environment where diffuse degassing occurs. In the case of volcanic craters where there is not vegetation, biogenic CO_2 cannot be produce or be a significant source for the soil gas CO_2 reservoir. This case is totally opposite to that of diffuse degassing far away from active volcanic craters where biogenic CO_2 production can be relatively high and where deep-seated CO_2 can rise through permeable structures. This scenario might account for a mixing process between two components with different concentrations and isotopic compositions. Therefore, a mixing process between a biogenic signature and a minor volcanogenic contribution of CO_2 might also account for the observed carbon isotope signatures of the soil CO_2 at Rabaul caldera.

Conclusions

Relatively anomalous soil gas CO_2 up to 20% have been observed where high levels of seismic activity have been taking place since the unrest of Rabaul caldera. Carbon isotopic composition of the soil gases suggest mainly a biogenic origin for the soil gas CO_2 and CH^4, but a small contribution of deep-seated CO_2 might contribute to the observed range of the soil gas CO_2 carbon isotopic composition. This anomalous soil CO_2 gas at the seismic annulus may reflect a significant gas-flow through this structure; therefore, soil gas CO_2 monitoring in the seismic annulus could be quite important for the volcanic-seismic surveillance of Rabaul caldera.

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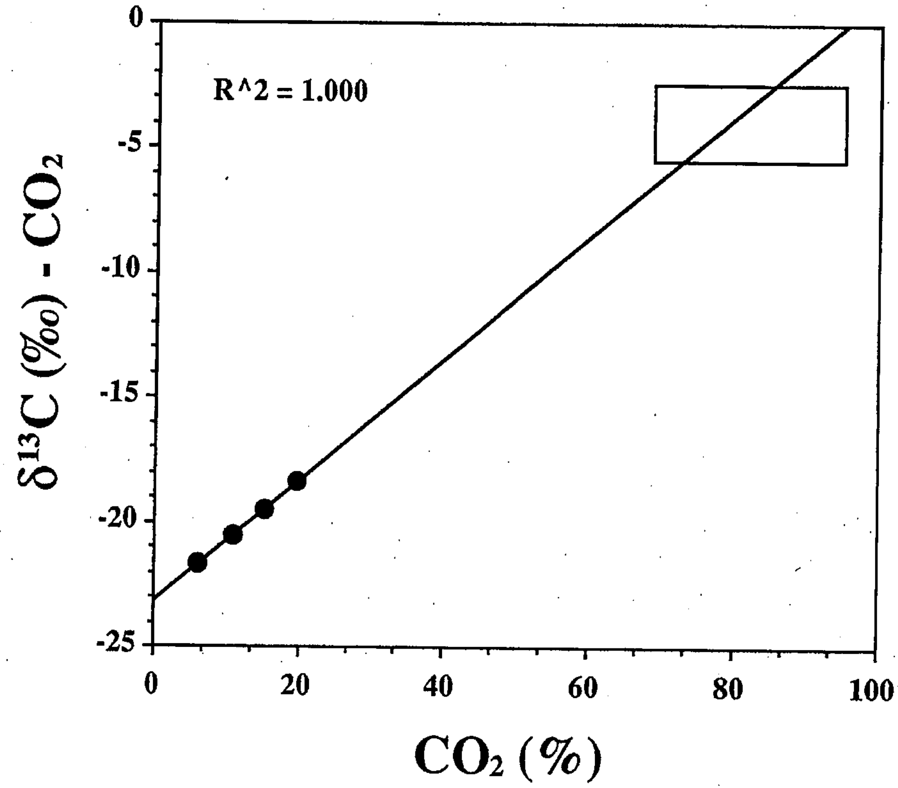

Fig. 4. Relationship between soil gas CO_2 concentrations and $d^{13}C$-CO_2 of samples which showed a heavier signature along the transect A-A' at Rabaul caldera. Correlation coefficient (1.000). Empty rectangle represent chemical and isotopic region values for volcanic-magmatic discharges at Rabaul caldera.

Fig. 4.- Relación entre la concentración de CO_2 de un origen no Biogenico y el $d^{13}C$-CO2en las muestras que indican una firma isotópica mas pesada a lo largo

Sample	CO_2 (%)	$\delta^{13}C$-CO_2 (‰ vs PDB)	$\delta^{13}C$-CH_4 (‰ vs PDB)
3	0.39	- 29.8	-
36	6.00	- 21.7	- 70.0
43	15.12	- 19.5	- 70.3
17	19.63	- 18.4	- 68.3
34	10.73	- 20.6	- 66.2
29	3.62	- 26.9	- 70.9

Table 1.- Carbon isottopic composition of soil gas CO_2 and CH_4 from Rabaul caldera, Papua New Guinea

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