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Continuous monitoring of distal gas emanations at Vulcano, southern Italy

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Abstract. The increasing activity of Vulcano Island (Italy) since 1985 led to the initiation of continuous geochemical monitoring of the lateral soil gas emissions. On the basis both of their relative geochemical characteristics and of local considerations, three gaseous components were selected for monitoring, namely CO_2, He and ^{222}Rn. Monitoring has been performed by means of specific analysers. Gases extracted from a water well located at the foot of the active cone were selected for monitoring, on the basis of their geochemical and isotopic characters that indicate their genetic link with central high temperature fumarolic gases emitted at the crater. Very strong variations of gas composition can be observed within one day (from 1 to about 94% for CO_2). Some variations display a daily character and can be correlated with that of atmospheric pressure. The three monitored gases are highly correlated, suggesting very high kinetics of gas transfer in the system. Because of these considerable variations of chemical composition, bulk concentrations obviously are not suitable for monitoring at Vulcano. However, the evolution with time of ratios such as $^{222}Rn/CO_2$ and He/CO_2 (the latter being corrected for atmospheric contamination) supplies numerical parameters that the expected to characterize the intensity of the degassing process. A new input of magmatic gases, that would lead to an increase in the $^{222}Rn/CO_2$ and He/CO_2 ratios, should therefore be detected by such a monitoring station.

Introduction

The geochemical survey of active volcanoes generally applies to those fluids which are related to crater degassing. A great deal of data has been obtained on fumarolic gas discharges from various volcanoes (e.g. Matsuo 1960; Mizutani 1978; Oskarsson 1984; Giggenbach 1987; Tedesco and Sabroux 1987; Tedesco et al., 1991). These data are of prime importance for identifying the volatile sources and the temporal fluctuations of degassing processes (Sabroux 1983). However, for surveillance purposes, crater gas emanations present obvious difficulties of either access or maintenance of equipment due to corrosion by acid gases. For this reason, although continuous data acquisition would be highly desirable to monitor the evolution of phenomena, only discontinuous survey is usually possible on such fluids. Only a few devices, such as permanent chemical sensors, have been developed for such a purpose (Gantes et al., 1983), but their life is limited by corrosion. For these reasons, attention has been recently devoted to the lateral emanations that occur by diffusion from volcanic piles. Such emanations, consisting essentially of carbon dioxide and rare gases, were initially recognized at an erupting volcano (Etna, Sicily; Aubert and Baubron 1988; Allard et al., in preparation), but were also detected at volcanoes in the dormant stage (Allard et al. 1988; Baubron 1988; Allard et al. 1989; Baubron et al., 1991). Being devoid of acid gases such as SO_2 and HCl, and occurring at safe distances from active craters, such emanations provide valuable conditions for continuous volcano monitoring. Soil gases have also been used successfully as geochemical precursors of earthquakes (King 1980; Del Pezzo et al., 1981; Reimer 1985; Sugisaki and Sugiura 1986).

The aim of this work was to test the validity of this approach to volcano monitoring at Vulcano, Southern Italy, where volcanic hazards are obvious. We report here the first results of 3-component (CO_2-He-^{222}Rn) monitoring of volcanic gases in a water well located at the base of the volcano.

Soil gas emanations at Vulcano

Vulcano Island is part of the active Aeolian volcanic arc, north of Sicily. Since its last eruption in 1888-1890,

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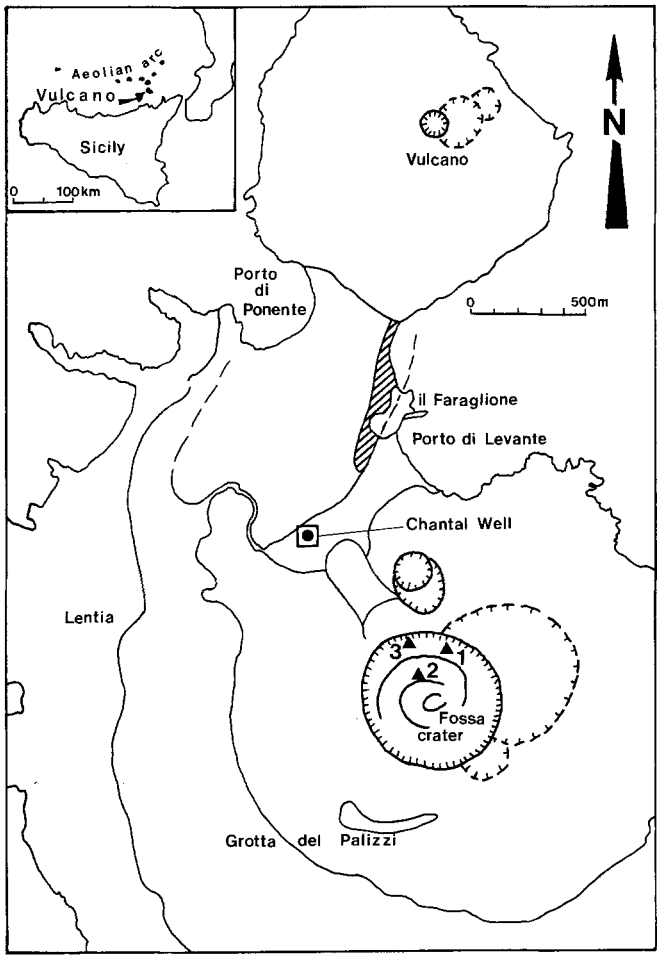


Fig. 1. Sketch map of Vulcano Island. Crater fumaroles location: *1*, F5 fumarole; *2*, Fa, crater pit fumarole; *3*, crater rim fissure fumarole

Vulcano has displayed mostly fumarolic activity, localized on the northern rim of the crater, and on the northern base of the active Fossa cone (341 m a.s.l.; Fig. 1). Fumarolic activity at the crater has varied strongly with time, with maximum fumarolic temperatures fluctuating between 200 and 600° C (Sicardi 1940; Martini et al., 1980; Martini 1989). Increasing fumarolic activity has been observed since 1978, and more recently since 1987. These manifestations are (1) increasing temperatures up to 550° C at some sites inside the crater, (2) increasing degassing rates, (3) the areal extension of fumarolic fields and (4) the opening of new fractures.

This situation led the Italian National Group for Volcanology (CNR) to promote a more intensive survey of Vulcano. Within this framework, the Osservatorio Vesuviano (Napoli) conducted an intensive programme of analyses of both crater fumaroles and soil gas emanations (Baubron 1989; Baubron et al. 1990; Tedesco et al., 1991).

Detailed prospecting of soil gases and atmospheres of water wells has revealed the occurrence of important gas leaks form the whole active cone and from a small area between this and Vulcanello (Fig. 1; Baubron et al., 1990). In some places, at the base of the cone, concentrations of up to 100 volume per cent CO_2 and 12 p.p.m.v. He were detected at 80 cm depth in the ground. Isotopic analyses of these gases confirm their volcanic origin, and their genetic link with the crater fumaroles (Baubron et al., 1990). CO_2-rich emanations, with the same chemical and isotopic characteristics, also occur in numerous water wells at the base of the cone. One of these water wells (the Chantal well - Fig. 1) has been selected as the best site for setting up continuous gas monitoring, for the following reasons:

1. It gives access to a deep exhalation (15 m depth).
2. Gas flows are significant (up to 1200 litres CO_2 per hour).
3. A clear relationship exists between gas in the well and that from the crater, as demonstrated by stable isotopes of carbon ($\delta^{13}C = -0.7$) and helium ($^3H/^4He = 5.2$ to 5.9 times the air ratio) in the well gas (Table 1).
4. Electric power is available for the equipment.

The monitoring was applied to the major component of the emanations (CO_2) and associated rare gases (He and ^{222}Rn). The interest in monitoring these three components and the methods used for their analysis have been described by Baubron et al., 1991.

We must remember that CO_2, after water, is the major species of volcanic gas and is one of the first gases to reach the surface of volcanoes, because of its very low solubility in shallow magmas (Stolper and Holloway 1988). Helium, although a trace component, is a more sensitive indicator of mantle-magmatic gas leaks owing to its higher isotopic ratio in the mantle than in the atmosphere ($1.4\ 10^{-6}$) and the continental crust ($< 10^{-7}$) (e.g. Lupton 1983). Finally, ^{222}Rn, owing to its short period of radioactive decay (3.8 days), provides some constraint upon the velocity of the gas transfer from depth to the surface (e.g. Tanner 1980).

Experimental procedures

Ordering of the station. The 3-component station is composed of a Diamant 6000 COSMA infrared analyser (IRA), and ASM 100 Turbo ALCATEL specific mass spectrometer (SMS), and a CD 23 SAPHYMOSTEL differential ionisation chamber (DIC), enabling the continuous measurement of CO_2 and He concentrations and ^{222}Rn volumic activity. Concentrations of CO_2 and He are measured with 0.5 and 2% accuracy respectively, and the activities of ^{222}Rn are measured with 10% accuracy (Baubron et al., 1991). This apparatus was successfully tested on Mount Vesuvius from June 1987 to September 1988 (Allard et al., in preparation). A similar station was used to monitor gases from fluids during deep drilling (3500 m depth, 18 months duration) in France (Baubron et al., 1987).

Figure 2 is a diagrammatic representation of the monitoring station. The water in the Chantal well is at a depth of about 15 m and has a temperature of about 60° C. The well atmosphere is continuously pumped at about 2 m above the water level, and introduced into the CO_2 analyser. Following the circuit, helium is intro-

Table 1. Chemical and isotopic results of gases sampled in the various summit fumaroles and in the water well. The location of fumaroles and well are indicated in Fig. 1. Both systems (crater fumaroles and water well) have similar chemical and isotopic characteristics, that suggest their common origin (Baubron et al., 1990)

	Selected crater fumaroles 1989			Water well 1988	Water well 1989
	Fissure	F5	FA		
Temperature (°C)	323	325	548	59	59
CO_2 (% vol)	92.3	84.4	79.5	93.5	46.0
He (ppm vol)	7.3	7.6	10.4	11.7	7.5
^{222}Rn (pCi/l)	2094	2309	1634	2070	1546
$\delta\ ^{13}C$	----- $-1<\delta\ ^{13}C<0$[1] -----			-0.7	n.a.
$^3He/^4He$ (R/Ra)c	--- $5.0<(R/Ra)c<6.0$[2] ---			n.a.	5.2–5.9[3]

[1] 1988 data (9 analyses of crater fumaroles)
[2] 1990 data (12 analyses of crater fumaroles)
[3] 2 analyses
n.a. Not analysed

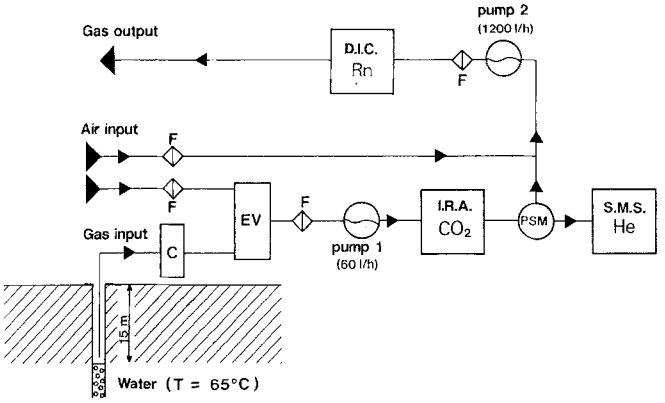


Fig. 2. Scheme of the analytical circuit. *D.I.C.* radon differential ionization chamber; *I.R.A.* carbon dioxide infra-red analyser; *S.M.S.* helium specific mass spectrometer; *PSM* permeation synthetic membrane; *C* condensor with automatic drain; *EV* electro-mechanical valves; *F* dust filters. *Arrows* indicate the direction of the flows

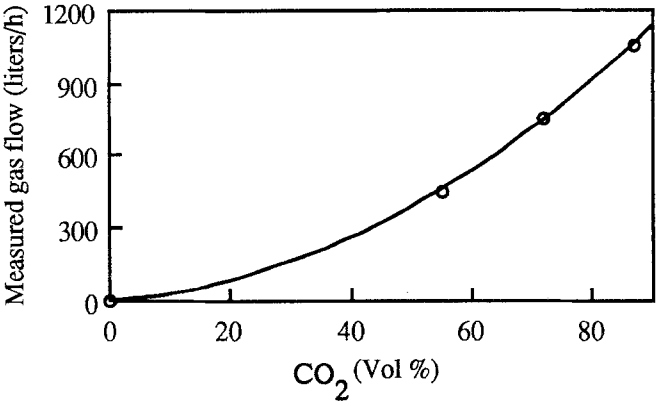


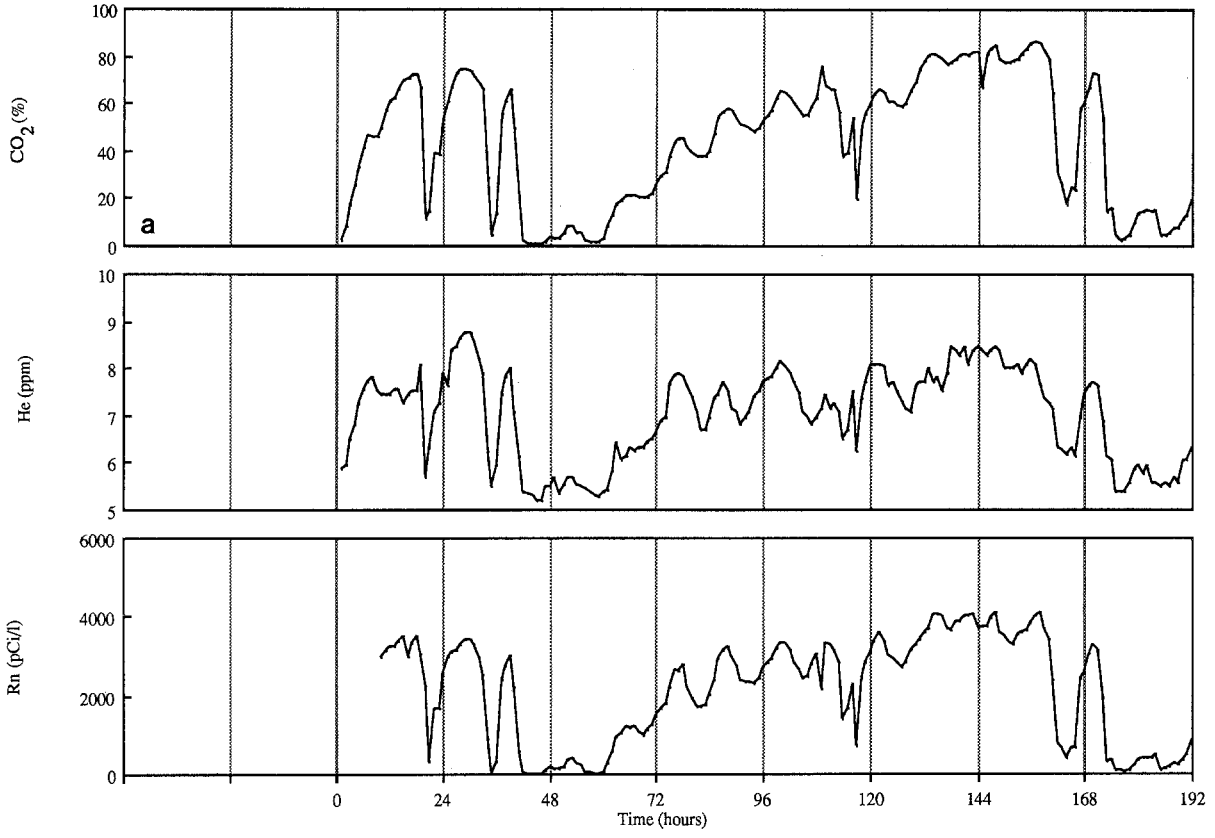
Fig. 3. Plot of the experimental flow values as a function of the CO_2 concentrations measured. For a concentration of zero, it is assumed that the natural flow is zero (with no experimental measurement)

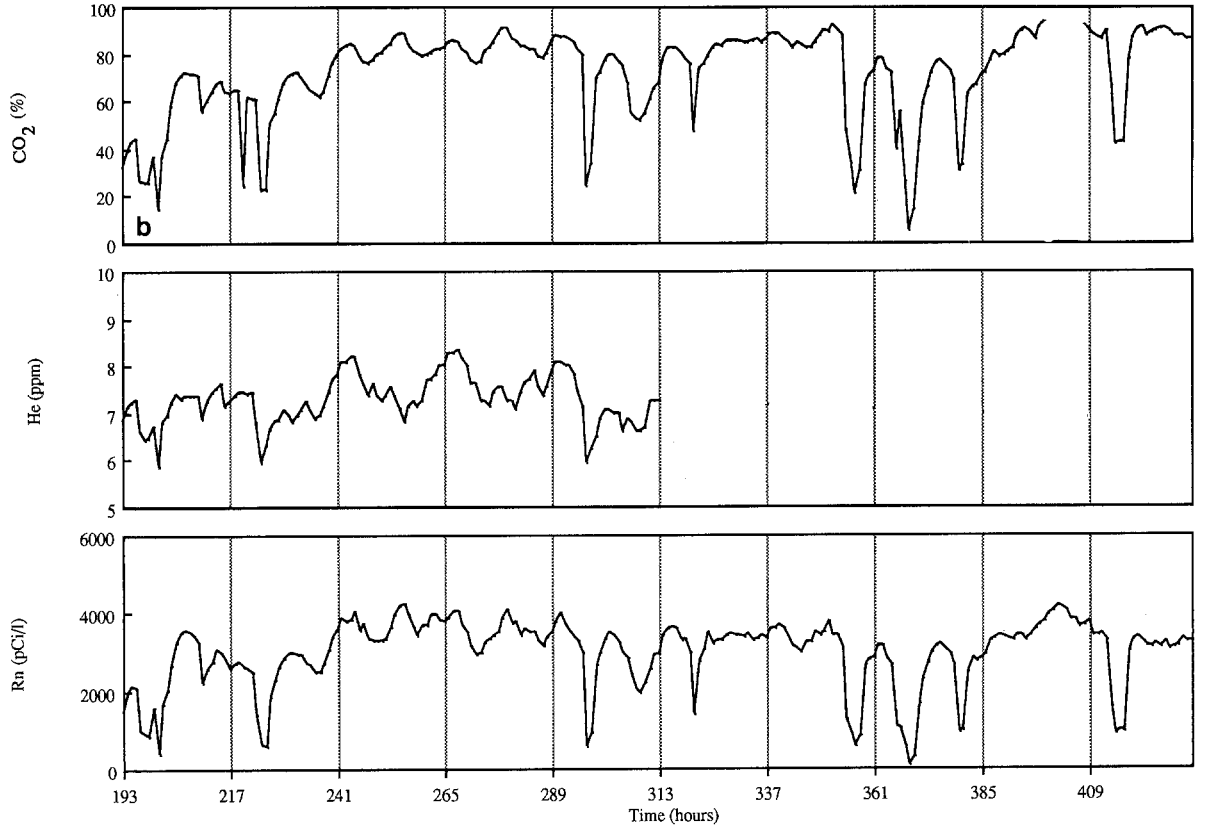
duced into the He specific mass spectrometer (SMS) after permeation through a synthetic membrane (PSM, Chevalier et al., 1974). The host gas is diluted (by a factor of 20) by air and then analysed in the ionization chamber (DIC). Electro-mechanical valves (EV) allow the alternate analysis of the gas in the well and of the outer atmospheric air, at 30 minutes intervals, in order (1) to compare the respective concentrations of CO_2, He and ^{222}Rn in the two samples and (2) to allow enough flushing of the ionization chamber from residual ^{222}Rn noise, the mean ^{222}Rn activity in the atmosphere (about 2 pCi/l) being very much lower than the volcanic signal by several hundred pCi/l. To dry the well gas, a water condenser with an automatic drain (C) was installed. Lastly, particles are trapped by filters (F). Calibration with gas standards for CO_2 and He analysers, and checking of the base line for the ionization chamber and filter cleanness were performed every 15 days. Data recording was first performed analogically, then numerically using a micro-computer connected to a specific 12 bit A/D conversion interface designed at IPGP.

Outflow of the water well. To select an acceptable outflow rate for monitoring, we have calculated the gas flow from the well for various concentrations. It is assumed that when natural flows are higher than an experimental extraction, the concentration measured does not change. When the experimental extraction is higher than the natural flow, air is input into the pipe, which lowers the concentration. In other words, a decrease of concentration indicates a natural flow lower than the extraction rate. Adjusting the flow rate to reach equilibrium between decrease and increase supplies the natural flow for the measured concentration. Figure 3 displays experimental flow values plotted against CO_2 concentration, which indicates a relatively low value of the maximum outflow of about 1200 liters CO_2 per hour for a 100% concentration. In order to minimize perturbations of the measured concentrations caused by extraction, a sampling flow of 60 l/h, which was also convenient for the CO_2 analyser, was selected.

Results

High concentrations and activities of the three monitored gases can be detected in the well (up to 93.8%


CO2 (%)
100
80
60
40
20
0
a
He (ppm)
10
9
8
7
6
5
Rn (pCi/l)
6000
4000
2000
0
0
24
48
72
96
120
144
168
192
Time (hours)


CO2 (%)
100
80
60
40
20
0
b
He (ppm)
10
9
8
7
6
5
Rn (pCi/l)
6000
4000
2000
0
193
217
241
265
289
313
337
361
385
409
Time (hours)

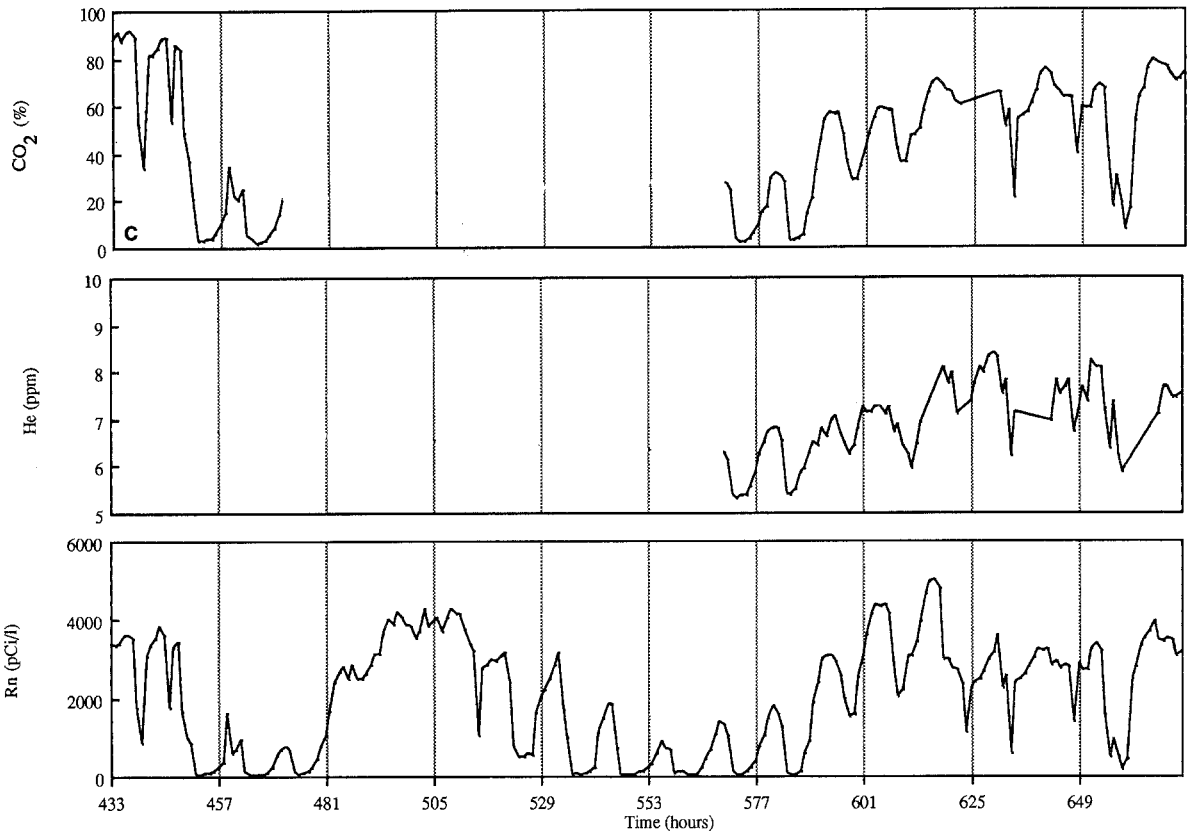


Fig. 4a–c. Continuous registration of CO_2 and He contents, and ^{222}Rn activity in the Chantal water-well atmosphere for a monthly period (3/3/89-31/3/89). Interruptions of the registration have occurred within this period, that are mainly due either to the breaking of the helium mass spectrometer filament or to a temporary bad working of the analogical recorder

CO_2, 9.12 ppm He and 5010 pCi/l ^{222}Rn). These values are very much higher than background values measured in non-active areas of Vulcano (Vulcano Piano, 3 km from the active cones), i.e. 0.25% CO_2, 5.2 ppm He and 100 pCi/l ^{222}Rn. Gas contents in the well fluctuate over an extremely wide range. For example, CO_2 can vary from about 1% to about 95% in a single day. Figure 4 shows a typical recording of the variations of the three components for about one month (3–31 March 1989). The two main features of this recording are the periodicity of the fluctuations and a direct correlation between the three gases. This can be seen more easily on Fig. 5.

Periodic fluctuations of the gas contents are obvious on Fig. 4 with a clear daily component (2 maxima per day) for most days, but also to a lesser extent with a longer wavelength (some days).

What are the transport mechanisms of the gases, and what is the mechanism that controls the periodic fluctuations of gas output? Three main factors can be suggested:

1. Water temperature. Weak fluctuations in water temperature (60–68° C) were recorded during a short period, in December 1988, without significant correlation with the CO_2 fluctuations.

2. Earth tide effects. Sugisaki (1981) and Sugisaki and Suguira (1986) reported that H_2 content and He/Ar ratios of bubble gases rising through mineral springs in Japan displayed clear correlations with earth tide, rather than with atmospheric pressure variations. They suggest that gas dissolved in mineral water at depth is squeezed out of fissures under tidal compression and rises to the surface through fault zones. This mechanism does not appear to account for the daily variations of the Chantal well, because no drift in time of the maxima and minima can be observed, even on the scale of a month (Fig. 4). Indeed, most of the maxima for the period 3–31 March are in the range 4.00–6.00 a.m. and 2.00–5.00 p.m., without apparent drift with time.

3. Atmospheric pressure effects. The effects of atmospheric pressure on outgassing of the system were investigated for a 10 day period, by measuring atmospheric pressure with a microbarometer, and the CO_2 contents of the well gas (Fig. 6). It can be seen that short wavelength (two maxima per day) variations of atmospheric pressure (in the range of a few mbars) and CO_2 are strongly inversely correlated, but that no proportionality coefficient can be related to these variations. The well-known fluctuation of atmospheric pressure as a function of local atmospheric temperature may account for the daily variations of gas contents in the well, as indicated by the fact that the two daily maxima occurred mostly at preferential times of temperature inversion. Nevertheless, no correlation has been observed between the long wavelength variations of CO_2 and atmospheric pressure (in tens of millibars). It

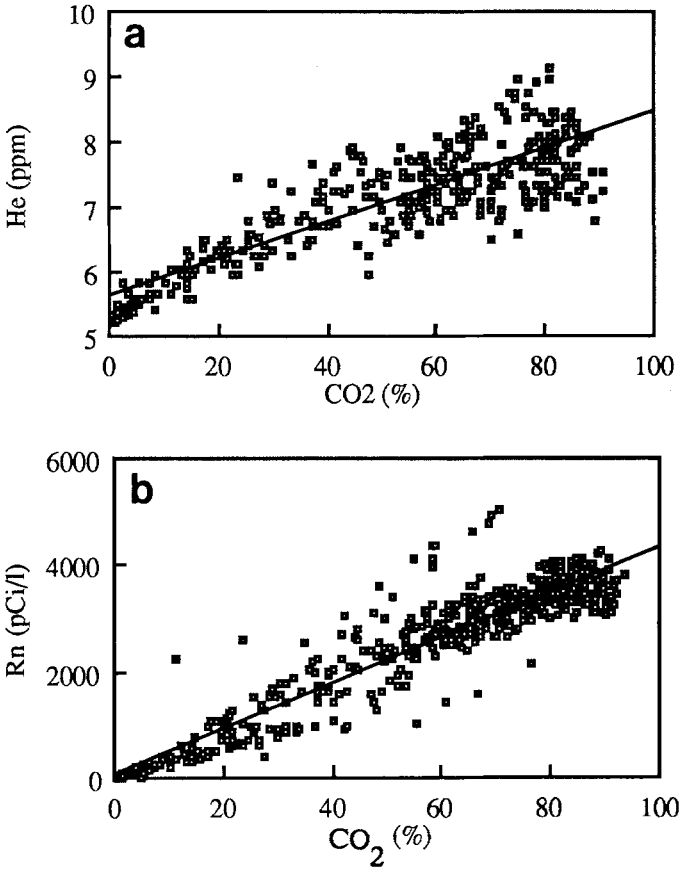


Fig. 5. Positive correlations between He and CO_2 (**a**) and ^{222}Rn and CO_2 (**b**), for a monthly period (3/3/89-31/3/89)

cannot therefore be ruled out that stress at depth, induced by long-period fluctuations in earth tide, may account for long-period variations of the CO_2 contents in the well. Long-term recording (about one year) should be carried out in order to perform harmonic calculations to investigate long-period earth tide influences.

According to these observations, and taking into account possible unknown long-period earth tide effects, it can be considered that slight changes in atmospheric pressure act on short period degassing. Such a dramatic effect is not unexpected when the relatively low calculated output rate of gases from the well (20 liters of CO_2 per minute, for a 100% CO_2 gas phase) is considered. The gases sampled 2 m above the water level therefore consist of a mixture of He and ^{222}Rn-bearing CO_2, and atmospheric air, through convection occurring in the well. The measured concentrations thus have the character of flow measurements.

Plotting the He/CO_2 ratio as a function of $1/CO_2$ (Fig. 7) illustrates the mixing between the atmosphere ($He/CO_2 = 1.5 \cdot 10^{-2}$) and the pure gas ($He/CO_2 = 8.4 \cdot 10^{-6}$) for the March recording. This is amplified for low concentrations of CO_2 by the fact that He increases more rapidly than CO_2, and decreases more slowly, probably as the result of the higher mobility of helium (due to its low solubility in water, monoatomic structure, chemical inertness and high diffusivity; Kahler 1981) with respect to CO_2.

The positive correlation of CO_2 and ^{222}Rn (Fig. 5b) suggest that the radon is carried out of the water by CO_2, in accord with the conclusions of Tanner (1980) who demonstrated that ^{222}Rn mobility is due to the mobility of its carrying fluid. Moreover, these direct correlations suggest that the kinetics of gas transfer through the superficial water system is very high.

Discussion

Because of their variability with time, it is clear that bulk He, CO_2 and ^{222}Rn contents cannot be used as geochemical parameters for continuous monitoring in Vulcano conditions. In contrast, ratios between these compounds may provide a geochemical tool for monitoring the global energy release from Vulcano.

Figure 8a is a plot of the bulk He/CO_2 ratios versus time. This gives scattered ratios too variable to be used for monitoring, clearly as the result of the mixing of He-bearing pure CO_2 with He-bearing atmospheric air. Helium concentrations in the total well gas release can be corrected for atmospheric contamination as follows:

$$He_{corr} = He_{measured} - He_{cont}$$

(where He_{cont} is the amount of He carried by atmospheric air in the well).

Assuming that the gas in the well is a mixture of CO_2 and atmospheric air, and that the atmospheric value of helium is 5.24 ppm (Gluechauf 1946), the helium contamination can be calculated as:

$$He_{cont} = (5.24 \times 10^{-2})(100 - CO_2)$$

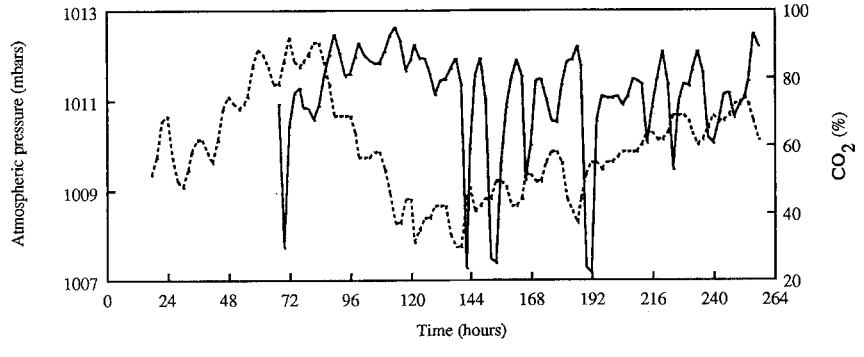


Fig. 6. Inverse correlation between the CO_2 content (volume %, *plain line*) of the water-well atmosphere and the atmospheric pressure (mbars: *dashed line*) for a 10 day period (17/5/89-27/5/89)

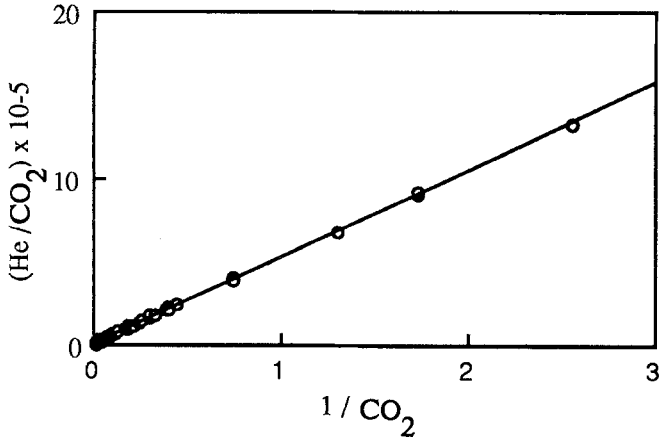


Fig. 7. Plot of the He/CO_2 ratio as a function of $1/CO_2$ content, for a monthly period (3/3/89-31/3/89)

The plot of He_{corr}/CO_2 versus time (Fig. 8b) displays little scatter, and may provide a useful baseline for quantifying the degassing state of the system. Monitoring this ratio should allow the detection of a magmatic input, that would be likely to increase the value of He_{corr}/CO_2 from its basic value (about 10^{-6}) towards typically mantle values of about 4.5×10^{-5} (Marty and Jambon 1987).

Figure 9 is a plot of Rn/CO_2 versus time, and shows little scatter. Because ^{222}Rn is expected to be a precursor of a rise in temperature of the groundwater due to an increase in the energy release of the volcano, monitoring $^{222}Rn/CO_2$ ratio in the well gas should also provide a valuable tool for detecting any new magmatic input.

Conclusions

This study shows that carbon dioxide, helium and ^{222}Rn, because of their diffuse emission through soils and wells in lateral parts of the volcano, are suitable gas species for long-term continuous monitoring of volcanic activity. At Vulcano island, such monitoring has been performed using specific analysers, with an automatic apparatus that has been installed in a water well selected on the basis mainly of chemical and isotopic characteristics.

Absolute concentrations of CO_2 and He, and ^{222}Rn activities have been found to vary strongly with time, probably as the result of short-period fluctuations of atmospheric pressure for the daily component. They

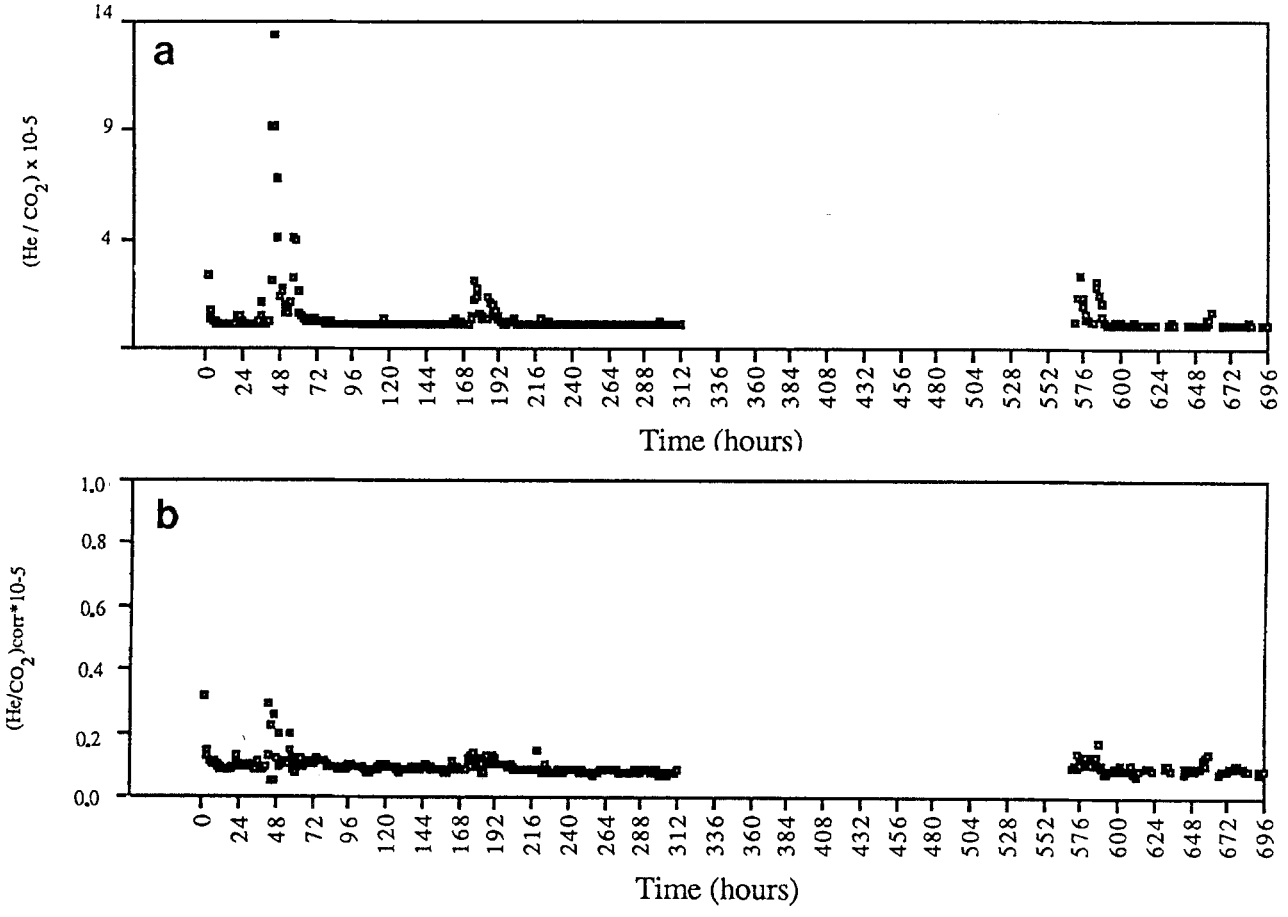


Fig. 8. Plot of the bulk He/CO_2 (**a**) and of the (He/CO_2) corr (**b**) corrected from the atmospheric contamination versus time, for a monthly period (3/3/89-31/3/89)

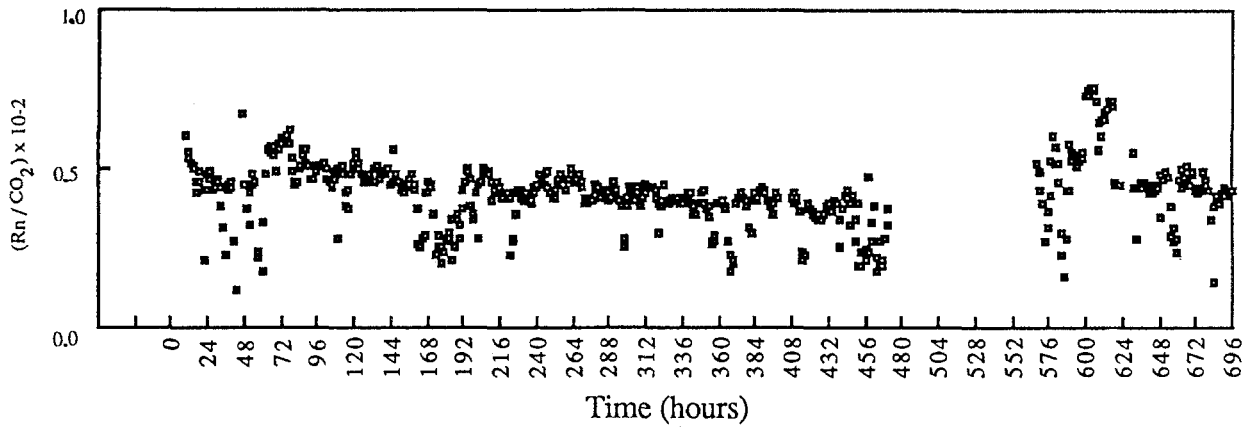


Fig. 9. Plot of the ratio Rn/CO_2 (b) ratios versus time, for a monthly period (3/3/89-31/3/89)

alone are therefore unsuitable fo continuous monitoring.

Nevertheless, geochemical considerations indicate that He/CO_2 ratios corrected for atmospheric contamination, as well as $^{222}Rn/CO_2$ ratios, should provide quantitative geochemical parameters characteristics of the state of activity of the volcano. Such data can be easily radio-transmitted, and a monitoring station of this type is therefore expected to constitute a performant tool for volcano monitoring.

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