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Water chemistry and soil radon survey at the Poas volcano (Costa Rica)

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Abstract

Radon-in-soil monitoring at the Poas volcano (Costa Rica) has been performed together with water chemistry from the hot crater lake since 1981 and 1983 respectively. The results are discussed as a function of the eruptive evolution of the volcano over a 13 years period (1981-1994). It is shown that no definitely clear precursory radon signals have been recorded. On the contrary, ionic species concentrations are likely to be considered good precursors, together with the temperature variations of the crater lake water.

Key words *Poas volcano – geochemistry – radon – precursor*

1. Introduction

The historical activity of the Poas volcano (Costa Rica) was observed and reported throughout the last century, showing periods of strombolian activity in 1910 and 1953-1955. Phreatic eruptions of geyser type, with plumes of water, gravel, mud and blocks originating from the principal crater lake were also reported (Barquero *et al.*, 1981; Casertano *et al.*, 1983).

Since radon-in-soil fluctuations and chemical variations observed in water bodies associated with active volcanoes may give information concerning the activity changes (Matsuo *et al.*, 1982; De la Cruz Reyna *et al.*, 1985, 1989; Not-su *et al.*, 1991; Brondi and Dall'Aglia, 1991; D'Alessandro and Parello, 1994; Dall'Aglia

et al., 1994; Tedesco and Pece, 1996), a radon-in-soil survey was initiated in 1981 and a systematic monitoring of the chemical composition of the hot water lake has also been implemented since 1983. In the present paper, we report the radon-in-soil behaviour together with the geochemical data obtained from the water sampling as a function of the volcanic activity and of its environmental effects during the 1981-1994 period.

2. Poas volcanic activity

The Poas volcano (10.20°N, 84.23°W) is one of the main active volcanoes of the Central Range of Costa-Rica, rising up to 2708 m a.s.l. (fig. 1a). It is located in the N.E. part of the Central Valley where the most populated cities of the country are also found.

The morphology of the summit presents two calderic structures with several cones such as Von Frantzius to the north and Botos to the south, where a cold freshwater lake is found. Prominent features of the active crater include a plain of eroded pyroclastic material to the south and a 30 m high cone formed during the 1953-1954 eruptions. The core of the cone consists of

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fractured lava of basaltic-andesitic composition; the northern portion of the cone is truncated by a pit crater which contains the acidic crater lake (Rowe *et al.*, 1992a,b).

The activity of the volcano during the in-soil radon monitoring period showed a quiescence phase since 1979 which lasted for several years. In June 1987, phreatic eruptions started and continued during the remaining part of the year, characterising a new activity phase of the volcano. The eruptions originated from the central and western part of the crater lake, ejecting water, sediments and gas columns. The water temperature rose from 58°C in January 1988 to 70°C in June.

The lake level decreased by 5 m during 1987. In April 1988, the ejecta column reached more than one kilometre height and the ejected materials affected particularly the southern flank. The lake level decreased by almost 40 m and the temperature fluctuated between 65 and 85°C. Fumaroles were also observed at the lake bottom with temperatures ranging from 75 to 98°C. Gas emission increased and the acidic rain affected areas of local economic importance such as coffee, grass, and other plantations. The sporadic phreatic activity continued during the year at a lower degree.

From April 1989, the activity intensified and the formation of a cone in the crater took

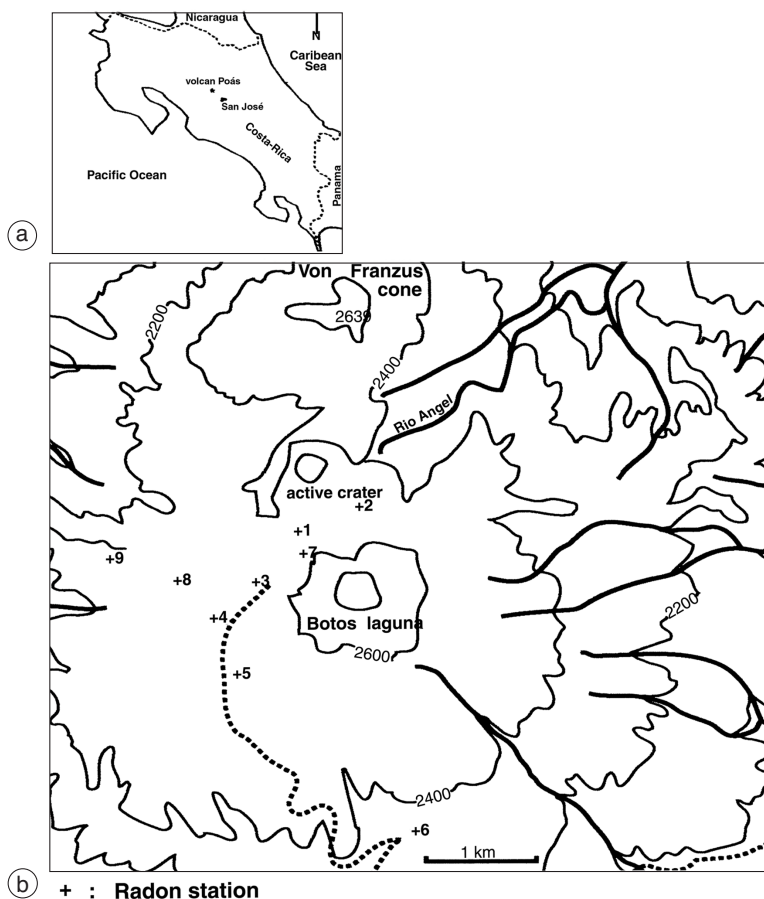


Fig. 1a,b. Location map of Poas volcano; radon network.

place with the ejected material. The crater lake disappeared at the end of the same month. On April 22th an eruption projected solid material 600 m away from the crater while on April 28th the sediments ejected from the lake bottom reached 2.5 km along the southern flank. On April 30th ash eruptions started and by May 1st the ash column reached one kilometre height. The crater lake recuperated during the rainy season. A phreatic eruption occurred at the end of May destroying the lake cone. From June 1989 to early 1990, the gas emanations were permanent with sporadic phreatic eruptions.

The crater lake disappeared again in April 1990. Eruptive activity was less intense than during the previous year, although ash falls reached 11 km on the southern flank around May 1990, affecting the cities of San Miguel, San Luis, Grecia and Trojas. Gas venting was observed at different locations of the crater with temperatures ranging from 90°C to 550°C. From 1990 to 1994 the activity continued at a lower rate, with the hot lake almost disappearing during the dry seasons.

3. Experimental

3.1. Radon measurements

Originally a radon-in-soil network consisting of 7 monitoring stations was set up in 1981, while two new stations were added in 1986 (fig. 1b). The monitoring has been carried out using Solid State Nuclear Tracks Detectors, LR-115 type 2 from Dosirad Co., France. The technique for exposure and detectors processing has been previously described (Seidel *et al.*, 1988). However, in brief, the set-up consists of a 1m long PVC pipe inserted in the ground which received a shorter 30 cm tube with an open bottom. Its upper bottom is closed and holds inside itself the polymeric Rn detector facing down. This shorter tube plays the role of a diffusion chamber. The remaining 70 cm upper part of the PVC tube is thermally insulated with rockwool and closed. By this means one measures actually the local radon flux across the Earth, which results after a while in a specific concentration within the diffusion chamber. Hence, data are expressed in kBqm^{-3} . The detectors were recovered essential-

ly on a fortnightly basis. However, due to logistic problems, *e.g.*, temporary inaccessibility, some of the detectors were recovered after different periods of exposure. The detectors were processed by batches in a NaOH solution and read by means of a jumping spark counter.

3.2. Chemical and physical data

Since 1983, temperature and pH measurements of the hot water lake have been performed monthly, together with water samples collection. Water samples were analysed for sulphates, chlorides and fluorides. Chlorides were quantified with a combination electrode (model 93-17, ORION) with a liquid membrane. The fluoride determination was performed with a specific electrode (model 96-07, ORION) and a Tissab buffer solution. Sulphates were determined by a modified turbidimetric technique from the American Public Health Association. The concentrations of the specific ions were quantified using analytical standard curves and the results are reported in ppm. The *pH* was measured with a Beckman 39820 combination electrode.

4. Results and discussions

Table I presents the average radon value and the 95% confidence limit ($2\sigma/n$), during the mon-

Table I. Average radon-in-soil concentration values ($X+2\sigma/n$) and uranium content in soil at the 9 monitoring stations.

Station	Radon (kBqm^{-3})	Uranium (ppm)	Rn/U a.u.
S1	7.8 ± 0.4	7	1.11
S2	1.5 ± 0.1	6	0.25
S3	0.96 ± 0.1	10	0.10
S4	1.9 ± 0.2	10	0.19
S5	1.0 ± 0.2	10	0.10
S6	1.4 ± 0.1	10	0.14
S7	1.5 ± 0.1	7	0.21
S8	1.6 ± 0.3	10	0.16
S9	3.1 ± 0.3	—	—

itoring period, and the uranium content of the soil at each station. Regarding stations 2, 3, 4, 5, 6, 7, and 8, the average radon concentrations show small variations and their ratio to the local uranium contents (expressed in arbitrary units) keep within a rather narrow range (0.10 to 0.25), indicating that the measured radon is either supported by the uranium in soil content or that the additional Rn flux is, on average, similar in intensi-

ty from point to point. This fact does not mean that Rn variations are not correlated with the activity of the volcano since it is well known that even when Rn signals are due to some deep phenomenon they show the modulation of in-soil Rn which originates from a small volume around the measuring site and is not from deep origin. The average Rn concentration as measured on these 7 stations is lower than 2 kBq m^{-3} .

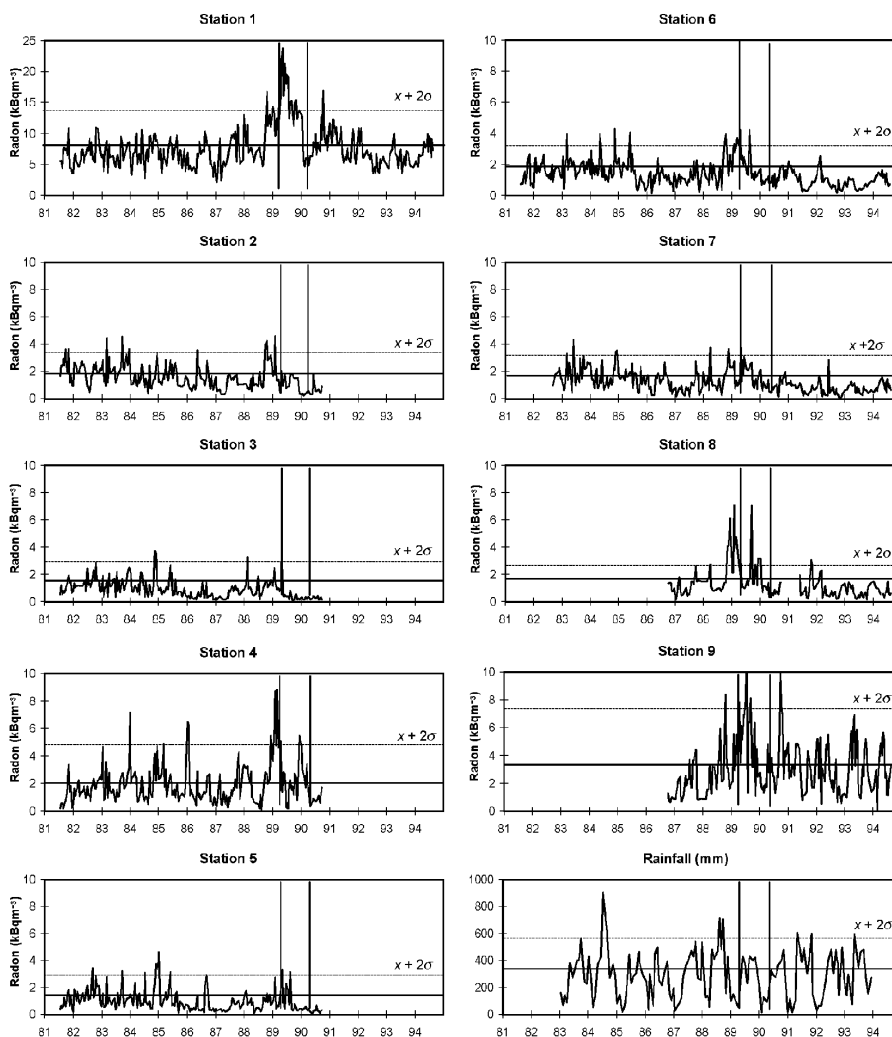


Fig. 2. Raw radon time series and rainfalls from 1981 to 1994 for the whole stations. The two vertical lines indicate the periods of hot lake disappearance.

On the contrary, on stations 1 and 9 the average is higher than 3 kBq m^{-3} . In addition, for station 1 located at the edge of the crater, the Rn/U ratio is substantially higher (1.11), indicating that an additional outgassing occurred on this site. U content on station 9, which is located in an altered zone, has not been measured.

The crude data recorded on the nine stations are exhibited in fig. 2, together with monthly rainfall recorded during the same period of time. At first site it seems that a strong peak appears particularly on station 1 in correlation with the 1989 eruption. However, before being able to make any data analysis some corrections must be made. It has been observed by several authors (*e.g.*, Fleischer, 1997) that the efficiency of the type of detectors used in this survey may vary, especially with the exposure time (ageing of the detectors and moisture). In order to account for this behaviour, on every station, the detectors were separated in several groups according to exposure time: 8 to 14 days (the most abundant) taken as reference; 1 to 7 days, 15 to 21 days and longer than 21 days. The average radon concentrations measured on every site for the above mentioned periods of times during 13 years (which legitimates the procedure) were calculated for a given period of time, namely 7 days. They have then be compared and related to those measured during the 8-14 exposure times. The corresponding multiplying correction factors are indicated in table II. The data have been corrected accordingly, keeping in mind that the effect of ventilation (when changing the detector) is negligible with respect to the loss of detector efficiency.

Only relative variations as a function of time have significance as possible precursory signals of an eruption. Accordingly, all the data were transformed, for the sake of comparison, under the form of centred and reduced values according

to the well established formula (*e.g.*, Bry, 1995)

$$z' = (z_i - \langle z \rangle) / \sigma_z$$

where $\langle z \rangle$ is the mean value and σ_z the standard deviation of a given set of z_i values of the Rn concentration. The same treatment was applied to rainfall data. The resulting Rn concentration and rainfall curves are exhibited in fig. 3.

The importance of the corrections carried out is clearly observed by comparing the two sets of data (figs. 2 and 3). On each set of curves, the 2σ horizontal line (which is commonly accepted as the criterion for an «anomalous» deviation) has been drawn. The two vertical lines show the time of the two lake disappearances in 1989 and 1990. For instance, if one focuses on the period of quiescence before 1989, several Rn peaks above the 2σ line are present. Among them, one is particularly «strong» around the end of 85-beginning of 86, on stations 3 and 4. After performing the correction, the «anomaly» on station 3 has completely disappeared. Another possible correlation can be observed in December 1984 at stations 2, 3, 4, 5, 6, 7. On all stations the anomalous peaks are still present after correction. Yet, they all occur at a time when the volcano was particularly quiet according to the observations of the Volcanological and Seismological Observatory of Costa Rica (Barquero *Ed.*, 1983/1987) and our own temperature and chemistry measurements (see below).

Over most of the sites atmospheric temperature and pressure variations do influence the in-soil Rn concentration. Before going further in the data analysis and discussion, it must be pointed out that it is not likely in this case since the environmental temperature ($19.2 \pm 0.8^\circ\text{C}$) and the atmospheric pressure ($779 \pm 0.66 \text{ mm Hg}$) are quite constant during the year, with very small night-to-day variations. A Fast Fourier Transform analysis of the

Table II. Correction coefficient calculated for each station, in function of the detectors exposure time.

Exposure	S1	S2	S3	S4	S5	S6	S7	S8	S9
1-7 days	0.31	0.58	0.34	0.34	0.23	0.38	0.38	0.49	0.43
8-14 days	1	1	1	1	1	1	1	1	1
15-21 days	1.22	1.20	1.32	1.41	1.20	1.20	1.13	1.06	1.19

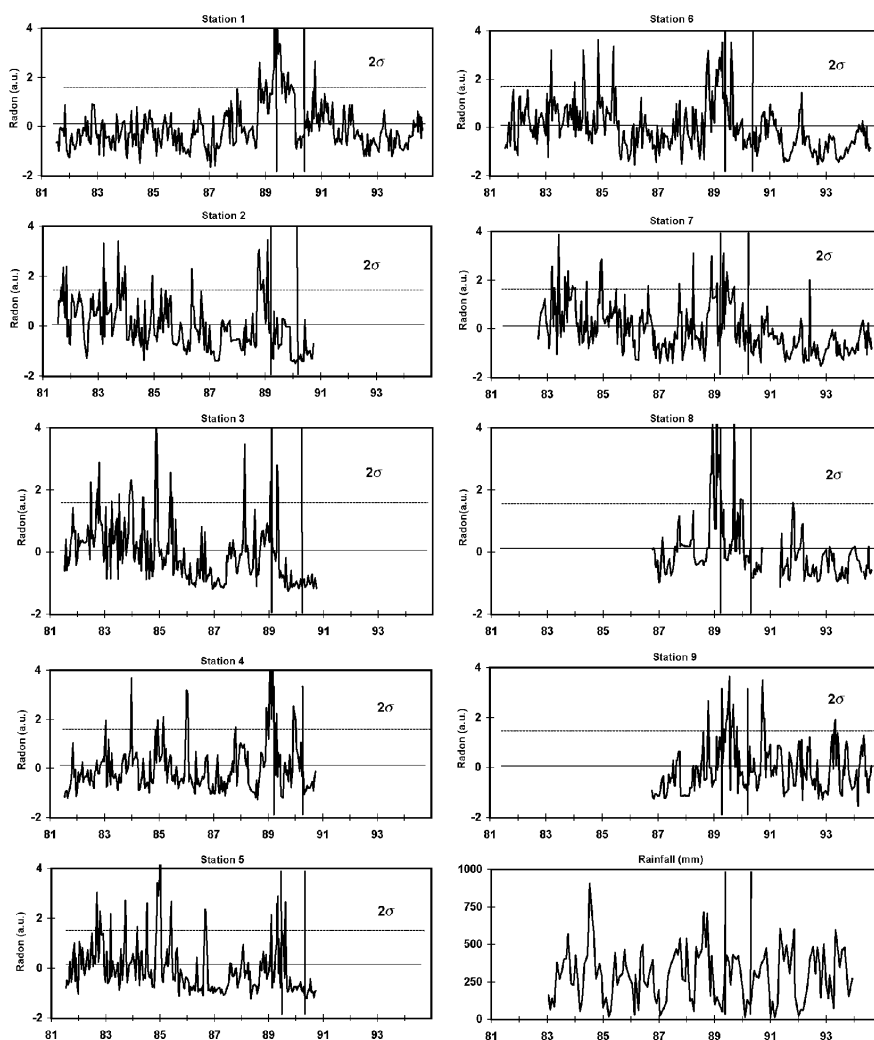


Fig. 3. Corrected radon time series and rainfalls from 1981 to 1994 for the whole stations.

radon time series shows a 365 days periodicity peak that corresponds to the precipitation pattern of the zone (rainy season from May to November and dry season from January to April). In general the rainy season exhibits the lowest radon-in-soil concentrations due to the water presence in the pores of the upper part of the soil. A radon increase occurs during the dry season for all the stations.

The conclusions that can be drawn from this data analysis are:

- i) Most probably, none of the «anomalous peaks» recorded during the present survey have any relation with volcanic activity.
- ii) Rn data from LR-115 type SSNTD detectors must be corrected for detection efficiency.
- iii) Rn concentrations measured on a long-term basis are mostly governed by rainfall.
- iv) If Rn precursory signals are to be found on such volcanic edifices, they must be sought using a short term Rn measuring probe such as the

one devised by Monnin *et al.* (1998). As a matter of fact such a device takes care of secondary effects such as external atmospheric parameters and it also detects short-term Rn outbursts that are likely to occur on volcanoes (Garcia *et al.*, 2000).

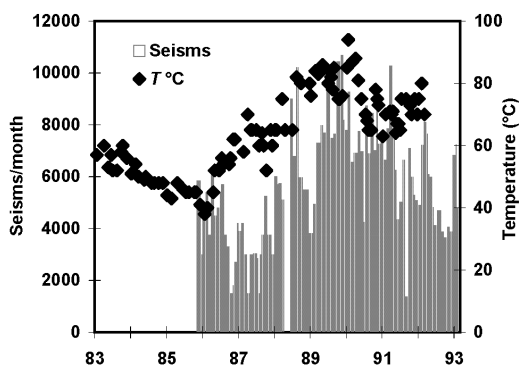


Fig. 4. Temporal variations of crater lake temperature ($^{\circ}\text{C}$) and local seismicity.

Nevertheless, if one focuses on the period when the volcano entered an active phase until it went into a quieter period, strong anomalous peaks can be observed at stations 1, 2, 3, 4, 5, 6, 7, 8 and 9. These peaks could be governed by rainfall but we would like to point out that all stations responded to the increase in activity of the volcano and also that the amplitude of the peaks are substantially higher than «dry-season» induced peaks observed previously. It could be said that both phenomena, the drying of the soil and the volcanic activity both contributed to the excess Rn release.

Figure 4 shows the evolution of the hot lake water temperature during the 1983-1993 period. From January 1983 to June 1986, the temperature was quite stable (around 49°C). From July 1986, the temperature increased, reaching a maximum (94°C) in July 1990. Seismicity also correlates with the eruptive pattern, increasing and reaching a maximum during the 1989-1991 period.

The variations of SO_4^{2-} , Cl^- and F^- concentrations of the hot crater lake water samples are shown in fig. 5. The results obtained by other

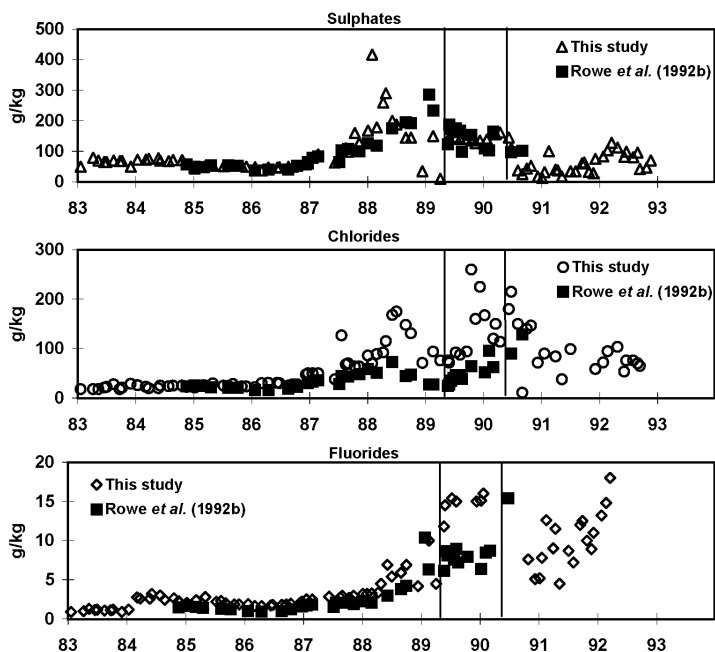


Fig. 5. Variations of SO_4^{2-} , Cl^- and F^- concentrations.

investigators (Rowe *et al.*, 1992a,b) are also shown in the same figure. Having such a double set of data covering the same period (November 1984-September 1990) and extending sideways for our data to January 1983 and to March 1993 allows us to draw some conclusions. From the end of 1984 to the beginning of 1988, the two sets of data are remarkably similar regarding in both concentration values and the behaviour of the ions. The two surveys confirm each other.

SO_4^{2-} , Cl^- , F^- and temperature measurements exhibit a stable behaviour from January 1983 to the end of 1986, with a lag time of 6 months with respect to the temperature increase which started in March 1987. A sharp increase then occurred by mid-1986 for all the ionic species. This behaviour is equally observed in Rowe and co-workers' report and in the present work.

The highest concentrations were measured during the first lake disappearance in April 1989. Then if the general behaviour is similar to Rowe and co-workers' report and ours, large discrepancies are observed in concentrations values. In other words, our chemical analysis data are affected by a large dispersion. These differences can be attributed to the mere fact that at this time the distribution of the ionic species in the lake was per-

turbed and also because sampling was not performed exactly at the same place, or at the same times by the teams of investigators. What remains nevertheless and, as a common finding, is that:

– Regarding sulphates: there is an increase that reaches its maximum before the April 1989 eruption and lake disappearance; followed by a general decrease till the beginning of 1991 *i.e.* 6 months after the second eruption and lake disappearance. Our data continue and show another increase starting in March 1991, reaching a maximum in February 1992 to decrease to a very low value at the end of the survey at the beginning of 1993.

– Regarding chlorides: there is an increase, more marked at our samples than at those of Rowe and his co-workers, but at the same time, with its maximum by mid-1988, followed in both cases by a decrease reaching its lowest values right before the 1989 eruption. Then again the chloride concentration increases, all the way after the second eruption. Then, our data show a slow decline of the Cl concentration till 1993.

– Regarding fluorides: we again observe values that are higher than those of Rowe and his co-workers but that exhibit the same behaviour *i.e.* an increase reaching maximum values between the two eruptions, followed by an erratic

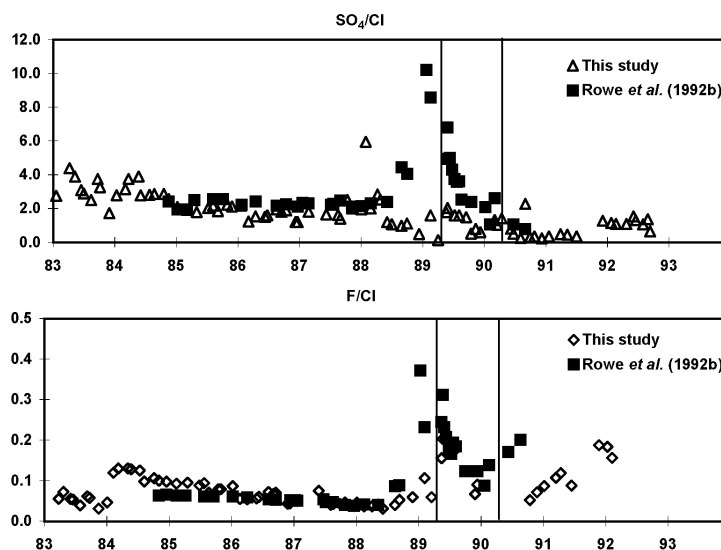


Fig. 6. $\text{SO}_4^{2-}/\text{Cl}^-$ ratio and F^-/Cl^- ratio.

decrease, then, as in the case of chlorides, a maximum but finally ending in an erratic distribution up to 1993.

Out of these results it could be said that the eruptive phase of the Poas volcano started in depth, when the temperature of the lake water started to increase 3 years before the actual eruption. The ionic activities in the lake confirm the start of the eruptive phase, the ion species being brought up to the level of the lake, as was suggested by Rowe *et al.* (1992, 1995), by the circulation of a hydrothermal fluid convection.

However, when one looks at the chloride based element ratios, it seems that it cannot be concluded that a SO_4^{2-} peak occurred before the 1989 eruption. Figure 6 displays the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio values obtained by the two teams are displayed. The peak observed by Rowe and his co-workers does not show on our data, or at least is barely marked (one point that looks more as being out of the statistics that having a genuine meaning). Regarding the F^-/Cl^- ratio (fig. 6), the behaviour is more in agreement in the two surveys, yet with a difference of two months at least for the time of maximum value. However, we observe a comparably high ratio long after the second eruption, in 1992 *i.e.*, 2 years later after a time when the volcano was going into a period of quiescence.

In the specific case of the Poas volcano and for this very eruptive phase, it is tempting to conclude that the precursory signal of the volcanic activity is the increased concentration of the ionic species, which is enhanced by the decrease of the lake volume, as Rowe *et al.* pointed out. This decrease of the lake volume is due itself (Brown *et al.*, 1989) to the evaporation from the lake surface caused by an increase in the power output attributed to the emplacement of a small magma intrusion inferred from microgravity measurements (Rymer and Brown, 1989). However, because of the large dispersion of the data, one cannot really rely on the chloride based ratios to estimate the imminence of the eruption.

5. Conclusions

The radon survey reported in this paper shows that radon data should be taken with great

care. After appropriate corrections, this survey neither shows nor allows us to conclude positively that any precursory signal was observed at the measuring stations prior to the eruptive phase 1989-1990. It could have been expected that some Rn excess could show at the stations located within the area of acidic rain since radon and HCl have similar properties regarding their solubility and water/air fraction ratios. It is not the case. Rn activities are similar in all the stations including station 6 which was located out of this area and which does not show any Rn depletion with respect to the other stations that were included within the area of acidic rain. It seems that long exposure Rn measurement by means of SSNTD is not suitable for this type of survey and that automatic short term Rn measurements should be preferred.

The hydrochemical survey shows that an increase in all the species measured is definitely related to the volcanic activity but that the chloride-based ratios should be taken with great care because of the large dispersion of the data.

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