

Compositional changes in a fumarolic field, Vulcano Island, Italy: a statistical case study

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Abstract: The identification of compositional changes in fumarolic gases of active volcanic areas is one of the most important objectives in monitoring programmes. Together with information from seismic data and deformation, it provides key data to the formulation and management of emergency plans for populations living near active volcanoes.

Chemical data obtained from different fumaroles collected at Vulcano Island (Sicily, southern Italy) between 2000 and 2004 have been analysed statistically. The methodology has identified parameters able to elucidate the structure of the complex fumarolic field of Vulcano in the investigated span of time, notwithstanding the high data variability. The southern portion of the Tyrrhenian Sea was affected by an earthquake ($M = 5.8$, 40 km NE of Palermo) in December 2002. Abrupt outgassing on the island of Panarea occurred in November 2002 and Stromboli was significantly active from December 2002 to July 2003. The great geological instability of the area is thought to have had an influence on the variability shown by the data.

The time-dependent variations in the components of the data have been investigated using log-ratios. The H_2O – HCl – SO_2 subcomposition, for a limited set of fumaroles, has been used to check for log-contrast principal components to be considered as a monitoring tool of volcanic activity. Results obtained indicate that the compositional changes are a complex function of time, chemistry, temperature and space. ANOVA (analysis of variance) of log-ratios for which there is no time dependence has elucidated components subject to significant spatial variations across the fumarole field, due to changes in redox conditions, and components dominated by random variations.

The present study was designed to apply statistical methodologies in the investigation of the chemistry of a complex fumarolic field as exemplified by Vulcano Island. The involvement of several possible sources in the chemical composition of volcanic gases and their modification in time and space often requires the use of explorative and inferential statistical tools. In this way systematic behaviours related to time and/or space may be distinguished and significant geochemical parameters able to characterize the evolution of the volcanic system identified. Furthermore, statistical methodologies are useful in characterizing the high chemical variability that potentially affects these systems, where several phenomena tend to combine and overlap each other, there is the presence of groups of observations with similar compositional behaviour, or the compositional patterns depend on time and/or temperature (Mazor *et al.* 1988; Chiodini *et al.* 1995; Montegrossi *et al.* 2001; Leeman *et al.* 2005). Adequate models of the compositional evolution of the fluids need to take into account the features of the sample space. The special and intrinsic feature of compositional data is that the proportions of a composition are

naturally subject to a unit-sum constraint. Volcanic gas chemistry is typically a composition where the parts are expressed in $\mu\text{mol mol}^{-1}$. In the investigation of volcanic gas chemistry the unit-sum constraint has been ignored widely or wished away. Consequently inappropriate standard statistical methods, devised for a successful application to unconstrained data, have been used with possible negative consequences in the interpretation of the information contained in a gas chemical composition. Here, the original, largely intuitive, approach to compositional data analysis formulated by Aitchison (1986), based on the use of log-ratios, has been followed. Recently, several theoretical developments point to a mathematically correct statistical approach to managing constrained data (Aitchison 1999; Pawlowsky-Glahn & Egozcue 2001; Von Eynatten *et al.* 2002; Egozcue *et al.* 2003). The power of the log-ratio approach has, furthermore, been demonstrated in the investigation of several problems in the Earth Sciences (Reyment & Savazzi 1999; Pawlowsky-Glahn & Buccianti 2002; Von Eynatten *et al.* 2003a,b; Buccianti & Esposito 2004; Buccianti & Pawlowsky-Glahn 2005).

Volcanological and geochemical background

The Aeolian archipelago (Sicily, southern Italy) is situated in the southeastern part of the Tyrrhenian Sea, some tens of kilometres off the northern coast of Sicily. It is related to the complex geodynamic situation of the Mediterranean area characterized by the collision between the African and Eurasian plates with N–S to NNW–SSE trending converging over the past 70 Ma (Frepoli *et al.* 1996). Vulcano is the southernmost of seven volcanic islands that form the Aeolian archipelago and it is one of Italy's active volcanoes (Barberi *et al.* 1974; Beccaluva *et al.* 1985; DeAstis *et al.* 1977). Vulcano, together with Lipari, is situated along a NW–SE tectonic alignment which transversely intersects the arc, coinciding with the structural line known as the Tindari–Letojanni lithospheric fault, with right-lateral strike-slip movements.

The last eruption of Vulcano dates back to 1888–1890, with the main event being located in the crater named La Fossa. Since then, the main fumarolic field, located on the northern inner and outer flanks of the La Fossa crater, covering an area of about 9000 m², has exhibited particularly high variability with regard to total gas emission rates and location and composition of the gas discharges (Chiodini *et al.* 1992). During the last 100 years, the outlet fumarole temperatures have varied from 600 °C in 1923 (Sicardi 1940) to less than 250 °C at the end of 1970 (Chiodini *et al.* 1992). Since 1978 fumarolic activity has been modified strongly, with temperatures increasing up to 700 °C (Chiodini *et al.* 1993; Martini 1993). At the present time outlet fumarole temperatures are around 400 °C.

The first chemical data for fumarolic discharges were reported by Sainte-Clare Daville (1856) and Fouqué (1856). Over the last three decades a number of studies have yielded large sets of chemical data from fumarole gas emissions, thermal waters and soil gases of the island (Martini & Tonani 1970; Shinohara & Matsuo 1986; Badalamenti *et al.* 1988; Baurbon *et al.* 1990; Minissale 1992; Panichi & Noto 1992; Bolognesi & D'Amore 1993; Martini 1996; Montalto 1996; Capasso *et al.* 1999, 2001; Di Liberto *et al.* 2002). Only since 1980 have geochemical models of the physical and chemical properties of the crater-gases been proposed and discussed (Martini 1980, 1983) by considering in addition seasonally induced variations that may perturb the primary volcanic signals. One of the main features of the different models is the role of a shallow aquifer located between the magma chamber, at a depth of about 4 km and the surface, controlling the thermal output and the chemical composition of the fumaroles. Carapezza *et al.* (1981) proposed a pressure

cooker model, inferring the presence of pressurized, two-phase (liquid–vapour) saline fluids in a reservoir at a depth of about 2 km, able to evolve along the boiling trend of a liquid with variable content of NaCl and CO₂ at about 350 °C. The dry model by Cioni & D'Amore (1984) proposed that the fumarolic discharges result from the variable mixing of (1) a deep magmatic component and (2) a shallower component (called marine hydrothermal) formed from the total evaporation of hydrothermal fluids (mostly water) of marine origin, the latter entering the low pressure, high temperature zone, which surrounds the uprising conduits of magmatic fluids affected by evaporation phenomena.

The great thermal variability of the Vulcano fumarole field has recently been proven by the results of detailed investigations for a large number of fumaroles carried out in May (end of the rainy season) and September (dry season) 2001 (Pirillo *et al.* 2002; Vaselli *et al.* 2003). In general, the fumarole discharges can be classified by their location and chemistry into outer and inner fumaroles with respect to the crater rim and fumaroles located on the crater rim itself. The outer gas discharges are located mainly along fractures that extend outwards from the rim and can reach temperatures up to 100 °C; their composition is generally water-dominated. The gases from the crater-rim fumaroles vary widely in temperatures (100–400 °C). Steam is still the main component, up to $98 \times 10^4 \mu\text{mol mol}^{-1}$, but high temperature gases (SO₂, HCl, HF, CO) become important. On the inner part of the crater rim, fumaroles display extremely high thermal and chemical variability, with temperatures ranging from 100 °C to 420 °C, indicating the presence of a complex situation. The wide-ranging behaviour suggests that only the monitoring of an elevated number of discharges over time may give information on the whole system. Consequently, seven fumaroles were selected as representative of the field and have been monitored from 2000 as follows: two from the outer part of the crater rim (labelled FNB and FZ), two from the rim itself (FNA and F5) and three from the inner part of the crater rim (F14, F27, F202). The aim was to identify geochemical parameters able to give simple indications about the chemical structure of the data and how the latter can be affected by temperature, time and/or space. The results can be used in subsequent plans of investigation focused on following changes in the behaviour of selected parameters and/or sampling sites.

Statistical analysis and results

The identification of significant changes in compositional data may be performed by taking into account the properties of the simplex, the

appropriate sample space for constrained data (data in which each of the components of the composition is a proportion of the fixed total). The chemical composition of volcanic gases (expressed in volume percentages, ppm, $\mu\text{mol mol}^{-1}$ or other related units) shows its variability in this sample space, a subset of real space, in which the application of standard statistical methods can lead to spurious results, confusing the underlying structure of the data, as well as producing wrong inferences. The chemistry of the gases for the fumaroles includes the following components: H_2O , CO_2 , SO_2 , H_2S , S, HCl, HF, N_2 , O_2 , H_2 , Ar, Ne, CO, CH_4 , C_2H_4 , C_2H_6 . Data were collected for 115 samples obtained from the fumaroles discussed above, during the period 2000–2004. Log-ratios of components were used to study patterns of variability (Aitchison 1982, 1986). The part that was put in the denominator is H_2O since it is the most important component of the composition and the main constituent of volcanic gases. It is involved in several key chemical reactions (e.g. $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, $4\text{H}_2 + 2\text{SO}_2 \rightleftharpoons \text{S}_2 + 4\text{H}_2\text{O}$ and $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$), all of which are highly dependent on temperature.

The temporal variation of both temperature and log-ratios has been studied for each fumarole. Time-dependence was examined using the

non-parametric Wald–Wolfowitz Runs Test, which evaluates random variation in sequences of data. The variable tested must be dichotomous, that is the values have to be below or above the mean or median values. This test is important since the assumption of mutual independence of successive values may not be sustainable in this case. Such lack of independence would preclude the use of several statistical inferential methods, which require this property in the data.

Temperature analysis

Probability plots of the outlet temperature gases from the seven fumaroles sampled between 2000 and 2004 are shown in Figure 1. Runs Test results indicate that successive data for each fumarole are independent of time ($\alpha = 0.05$). The Kolmogorov–Smirnov test for goodness indicates that the data have Gaussian distribution ($\alpha = 0.05$). Use of the Student *t*-test to compare means and variances shows that there are significant differences between all the fumaroles ($\alpha = 0.05$) with regard to the outlet gas temperatures. Consequently, outlet temperatures can be considered as being drawn from different populations with different mean values increasing from 100 °C (FZ, $n = 10$) to 211 °C (F5, $n = 13$), 247 °C (FNB, $n = 12$), 285 °C (FNA, $n = 15$), 306 °C (F14,

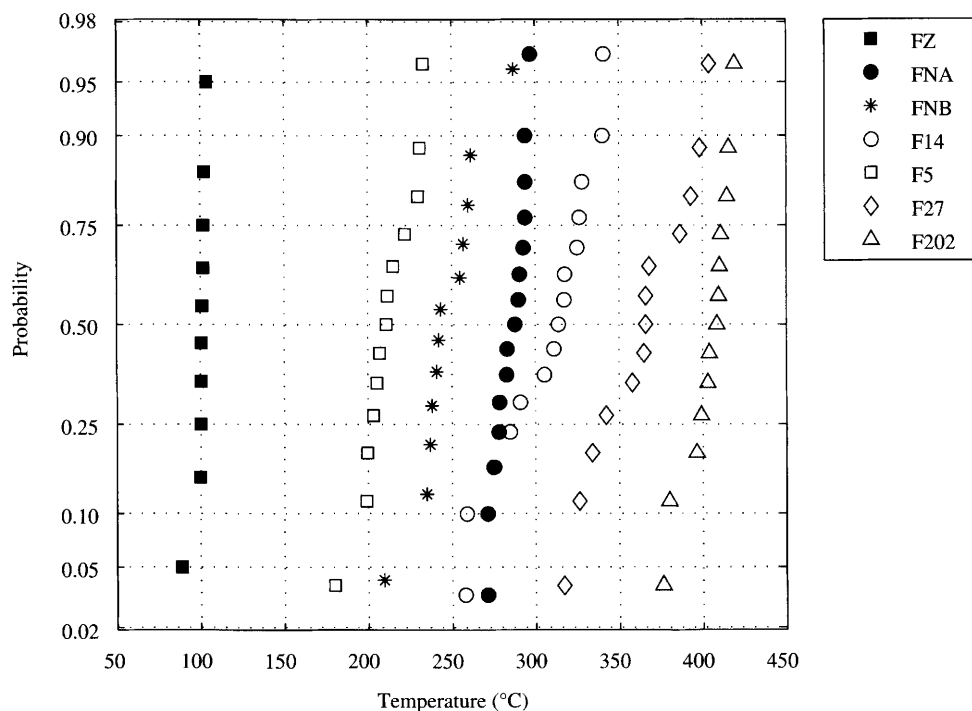


Fig. 1. Normal probability plots for outlet temperatures of the seven fumaroles.

$n = 15$), 363 °C (F27, $n = 13$) and 403 °C (F202, $n = 13$).

Log-ratio analysis

Log-ratios $\ln(\text{SO}_2/\text{H}_2\text{O})$ and $\ln(\text{HCl}/\text{H}_2\text{O})$ show patterns that are time-dependent and only for three fumaroles, as follows: F14 for $\ln(\text{HCl}/\text{H}_2\text{O})$, FNA for both $\ln(\text{SO}_2/\text{H}_2\text{O})$ and $\ln(\text{HCl}/\text{H}_2\text{O})$, FZ for $\ln(\text{SO}_2/\text{H}_2\text{O})$ ($\alpha = 0.05$). The temporal patterns of these log-ratios are shown in Figures 2 and 3. Other log-ratios show no time-dependence and, consequently, random variation is the dominant feature governing compositional changes. Analysis of variance (ANOVA) can be used to determine whether time-independent log-ratios are able to distinguish fumaroles. Kolmogorov–Smirnov tests have been carried out to verify for fit to the Gaussian distribution for each log-ratio ($\alpha = 0.05$). In addition, the value of the Levene statistic for the homogeneity of variance was calculated in order to test whether all the group (fumarole) variances are homogeneous. The results indicate that this hypothesis can be accepted for $\alpha = 0.01$.

ANOVA indicates that only the log-ratios $\ln(\text{H}_2/\text{H}_2\text{O})$, $\ln(\text{CO}/\text{H}_2\text{O})$, $\ln(\text{CH}_4/\text{H}_2\text{O})$ and $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$ vary significantly among the fumaroles,

independently of time. Thus, the spatial location appears to be the dominant feature governing the differences among F5, F27, F202 and FNB fumaroles for the values of these log-ratios. Box-plots of the values of the log-ratios for the four fumaroles are shown in Figure 4. Significant differences are present for: (1) $\ln(\text{H}_2/\text{H}_2\text{O})$, comparing F27 with F202 and FNB; (2) $\ln(\text{CO}/\text{H}_2\text{O})$, comparing F27 with F5 and FNB; (3) $\ln(\text{CH}_4/\text{H}_2\text{O})$, comparing F202 with F5, F27 and FNB; (4) $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$, comparing F27 with FNB, in all cases for $\alpha = 0.05$. Fumarole F27 consistently differs from the others for all the mentioned log-ratios.

For all the other log-ratios [$\ln(\text{CO}_2/\text{H}_2\text{O})$, ..., $\ln(\text{C}_2\text{H}_6/\text{H}_2\text{O})$] ANOVA results indicate that these gas components show no variations among fumaroles ($\alpha = 0.05$).

Subcompositional analysis

For the general form of a chemical reaction the corresponding equilibrium constant has an equivalent logarithmic form. The logarithmic version encourages the view that a sensible way to identify patterns in compositional datasets is to search for natural log-contrasts of the components of the composition (Aitchison 1983, 1999). The

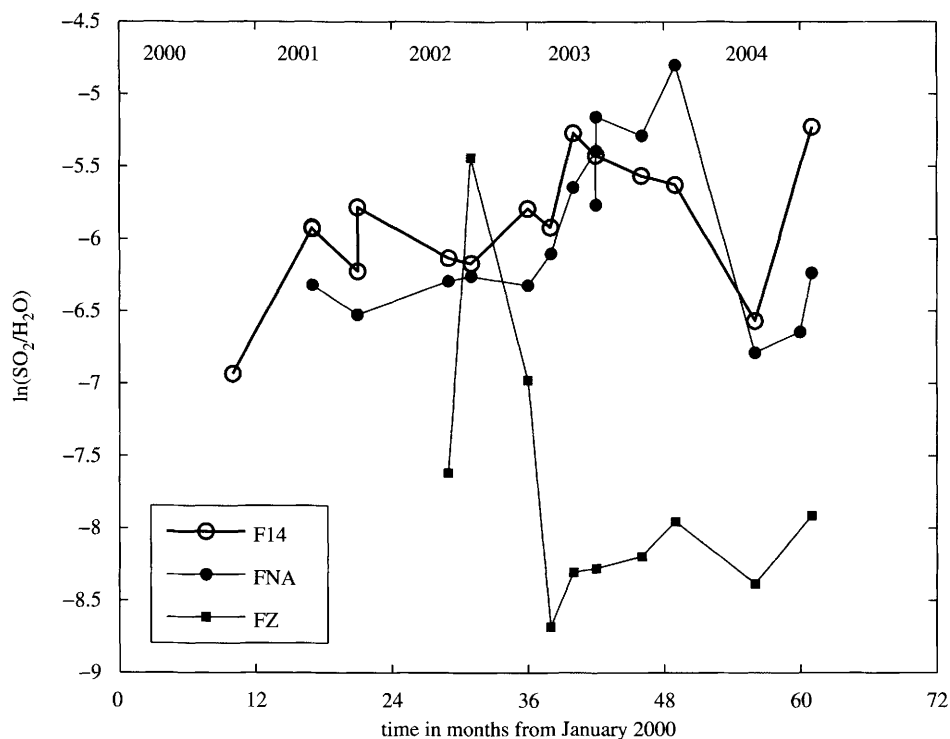


Fig. 2. Time behaviour of the log-ratio $\ln(\text{SO}_2/\text{H}_2\text{O})$ for fumaroles F14, FNA and FZ.

CHANGES IN A FUMAROLIC FIELD OF VULCANO

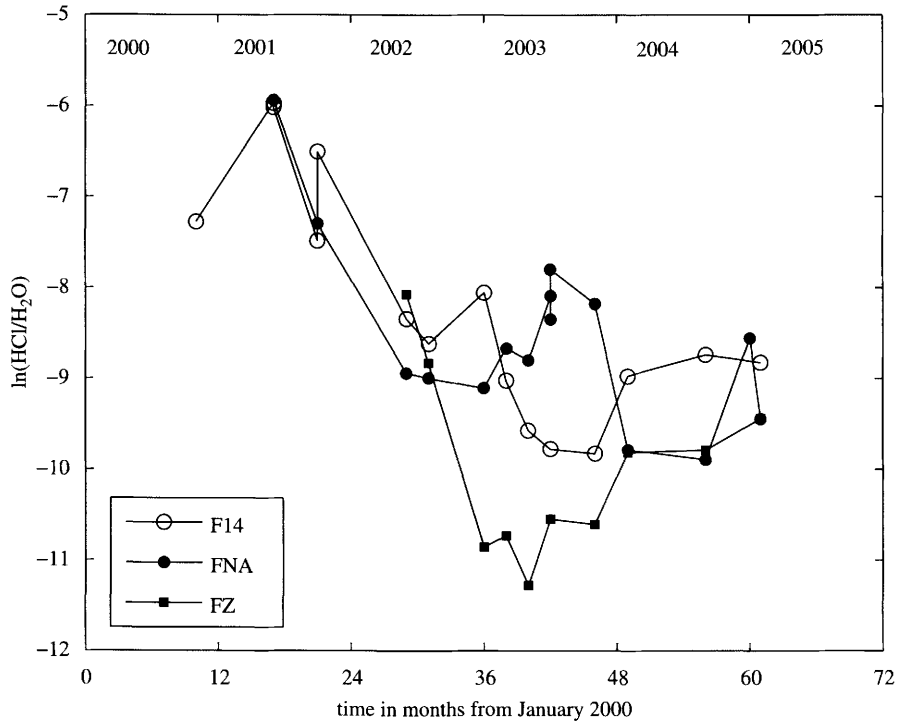


Fig. 3. Time behaviour of the log-ratio $\ln(\text{HCl}/\text{H}_2\text{O})$ for fumaroles F14, FNA and FZ.

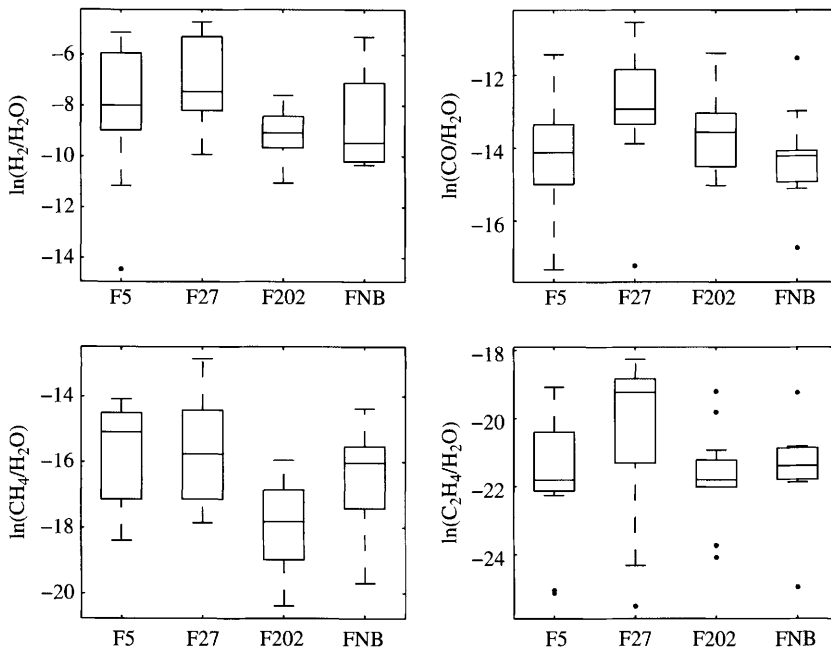


Fig. 4. Box-plots of the log-ratios $\ln(\text{H}_2/\text{H}_2\text{O})$, $\ln(\text{CO}/\text{H}_2\text{O})$, $\ln(\text{CH}_4/\text{H}_2\text{O})$ and $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$ for fumaroles F5, F27, F202, FNB.

time-dependent log-ratios, $\ln(\text{SO}_2/\text{H}_2\text{O})$ and $\ln(\text{HCl}/\text{H}_2\text{O})$, identify the subcomposition $\text{H}_2\text{O}-\text{HCl}-\text{SO}_2$ where the features of the log-contrast principal components can be checked. The aim is to find a simple relationships containing information about the evolution of the volcanic system. The centred log-ratio covariance matrix Γ as a means of specifying a compositional covariance structure and the concept of the log-contrast of a composition were used by Aitchison (1983) to provide a practical form of compositional principal component analysis. In this context, a log-contrast of a D -part composition \mathbf{x} is any log-linear combination $a_1 \ln x_1 + \dots + a_D \ln x_D = \mathbf{a}' \ln \mathbf{x}$ with $a_1 + \dots + a_D = \mathbf{a}' \mathbf{j} = 0$. The first log-contrast is given by the equation:

$$0.47 \ln(\text{H}_2\text{O}) - 0.81 \ln(\text{HCl}) + 0.34 \ln(\text{SO}_2) = k_1. \quad (1)$$

The proportion of the total subcompositional variability which is retained by the first log-contrast principal component is about 64% ($\lambda_1 / \sum_{i=1}^D \lambda_i$, where λ_i are the eigenvalues of Γ and D , the parts of the composition). Dividing each component by 0.81

and approximating the coefficients by 0.5, obtains:

$$\frac{(\text{H}_2\text{O})^{1/2} \cdot (\text{SO}_2)^{1/2}}{\text{HCl}} = \exp k_1. \quad (2)$$

for which k_1 can be calculated for each sample. A probability plot for k_1 values of each fumarole is reported in Figure 5. The position of the different cumulative curves clearly reveals the presence of the spatial variation from the inner part of the crater to the rim and the outer part. Furthermore, the increase in k_1 values is related approximately with time and with the decrease in temperature. These results clearly indicate that first log-contrast principal component is a complex function of chemistry, temperature, time and space. It can represent a statistical tool to monitor for processes that take into account about 2/3 of the subcompositional variability affecting the system. The processes involve H_2O , SO_2 and HCl in the proportion 0.5 : 0.5 : 1. The equation for the second log-contrast principal component (explaining about 36% of the subcompositional total variability) is given by:

$$0.67 \ln(\text{H}_2\text{O}) + 0.07 \ln(\text{HCl}) - 0.74 \ln(\text{SO}_2) = k_2. \quad (3)$$

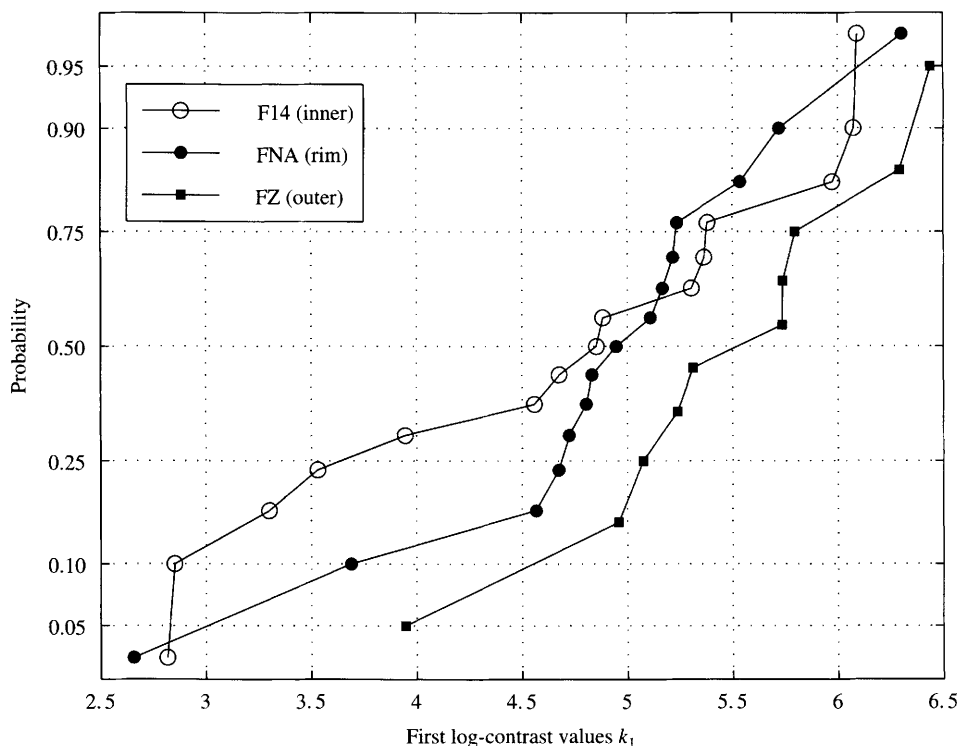


Fig. 5. Probability plot of the first log-contrast values k_1 discriminated by fumaroles.

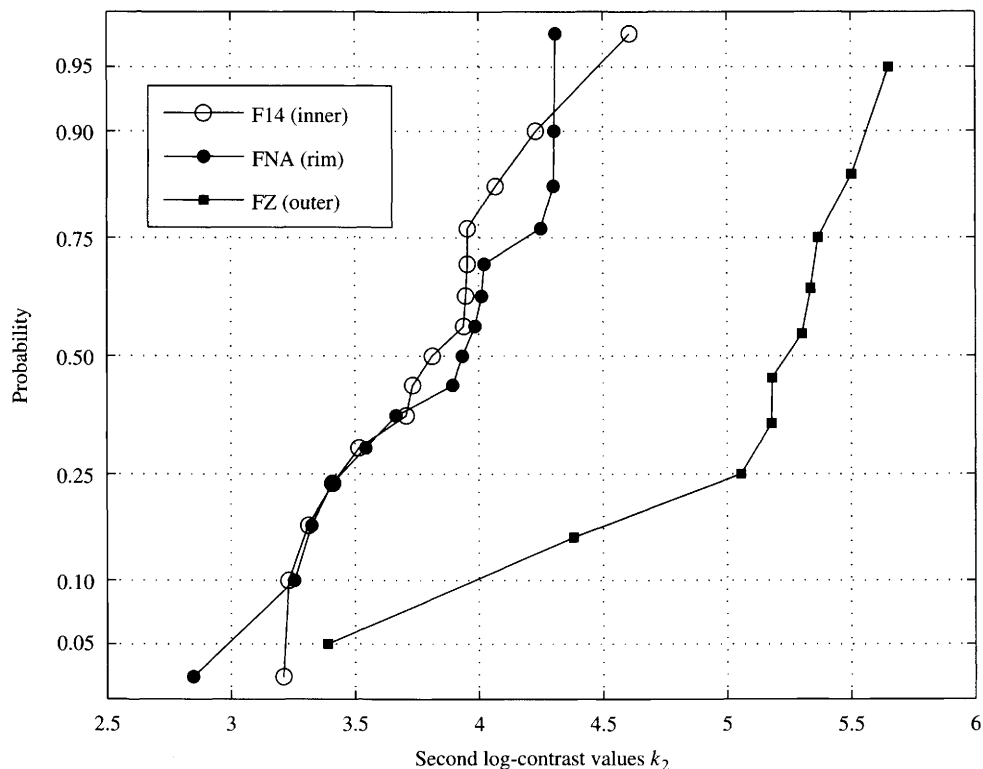


Fig. 6. Probability plot of the second log-contrast values k_2 discriminated by fumaroles.

Given that the coefficient for HCl is so low, equation (3) can be expressed as:

$$\frac{(\text{H}_2\text{O})^{0.67}}{(\text{SO}_2)^{0.74}} = \exp k_2. \quad (4)$$

A probability plot for k_2 values of each fumarole is reported in Figure 6. In this case too, the position of the different cumulative curves clearly reveals the presence of the spatial variation from the inner part of the crater to the rim and to the outer part. However, F14 and FNA fumaroles show a more similar behaviour with respect to the previous case and this appear to be related to the lack of HCl.

These results indicate that the second log-contrast principal component is a simple function of chemistry (only two variables), space (inner and rim parts of the crater discriminated from the outer one), temperature and time. The increase in its values is related approximately to time and to the decrease in temperature. Consequently, equation (4) can represent a useful tool to follow processes explaining about 1/3 of the data variability and related to H_2O and SO_2 .

Discussion

The geochemical–statistical investigation of the compositional data of fumaroles related to the field of Vulcano Island in terms of log-ratios with H_2O as the denominator reveals the presence of: (1) a time–space dependency for $\ln(\text{SO}_2/\text{H}_2\text{O})$ and $\ln(\text{HCl}/\text{H}_2\text{O})$; (2) a space dependency for $\ln(\text{H}_2/\text{H}_2\text{O})$, $\ln(\text{CO}/\text{H}_2\text{O})$, $\ln(\text{CH}_4/\text{H}_2\text{O})$ and $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$, associated with the discriminant behaviour of F27 fumarole; and (3) randomness in time and space for $\ln(\text{CO}_2/\text{H}_2\text{O})$, $\ln(\text{H}_2\text{S}/\text{H}_2\text{O})$, $\ln(\text{S}/\text{H}_2\text{O})$, $\ln(\text{HF}/\text{H}_2\text{O})$, $\ln(\text{N}_2/\text{H}_2\text{O})$, $\ln(\text{O}_2/\text{H}_2\text{O})$, $\ln(\text{Ar}/\text{H}_2\text{O})$, $\ln(\text{Ne}/\text{H}_2\text{O})$ and, finally, $\ln(\text{C}_2\text{H}_6/\text{H}_2\text{O})$.

In the first case, two acid gases (SO_2 and HCl) are involved. These species, along with HF, can be highly affected by scrubbing, as the magmatic gases rise to the surface (Symonds *et al.* 2001). The $\ln(\text{SO}_2/\text{H}_2\text{O})$ log-ratio changes significantly with time for FNA (rim) and FZ (outer), while the F14 (inner) trend is, instead, not significant from a statistical point of view, even if quite similar to those of FNA (Runs Tests, Fig. 2); are should notice here the wide oscillations characterizing the behaviour of FZ before 2003. By considering these features it may be concluded that either the

influence of the shallow environment has decreased in time from 2000 to 2004 or the magmatic contribution has increased (both in a significant manner) and that only on the rim and the outer part of the crater statistically significant changes in $\ln(\text{SO}_2/\text{H}_2\text{O})$ occur.

The behaviour of $\ln(\text{HCl}/\text{H}_2\text{O})$ over time (Fig. 3) is similar for the F14, FNA and FZ fumaroles at the beginning of 2002 and at the end of 2004. It diverges markedly at the end of 2002 for FZ and less markedly for F14 and FNA. However, it may be useful to remember that for FZ the revealed time pattern is not statistically significant. The behaviour of the log-ratio in the three fumaroles appears to reveal the presence of some general mechanism that is able to homogenize the data in time, independently of their spatial location. This type of phenomenon occurred at the beginning of 2002 and at the end of 2004. Data of different times have changed following more or less different evolutive paths, with respect to their spatial location. Fluctuations may be due to the different sources contributing HCl and, in particular, to secondary non-magmatic processes as, e.g. interactions of sea water with hot rocks leading to the formation of volatile HCl (Mazor *et al.* 1988). It is known that Vulcano fumaroles show a marine signature due to sea water that directly enters the hydrothermal system at shallow levels (Cortecci *et al.* 1996, 2001). Similarity among data drawn from different fumaroles can be related to periods of time in which an increase in fluids circulation smoothed the differences. The similar behaviour of the log-ratio $\ln(\text{HF}/\text{H}_2\text{O})$ appears to confirm this hypothesis.

The investigation of the subcomposition $\text{H}_2\text{O}-\text{HCl}-\text{SO}_2$ yielded two relationships that link the chemical species in a form similar to the Law of Mass Action. The first relationship, called first log-contrast principal component (2/3 of the total subcompositional variability), models the behaviour of chemical species able to give information on important phenomena as the magmatic contribution (SO_2), scrubbing (H_2O) and the extent of the water-rock interactions (HCl). The relationships among these processes can be quantified by the proportion 0.5 : 0.5 : 1. The second log-contrast (1/3 of the total subcompositional variability) models mainly changes in the $\text{H}_2\text{O}/\text{SO}_2$ ratio and, consequently, scrubbing phenomena compared with the magmatic contribution.

If the behaviour of the log-ratios depending only on space, as $\ln(\text{H}_2/\text{H}_2\text{O})$, $\ln(\text{CO}/\text{H}_2\text{O})$, $\ln(\text{CH}_4/\text{H}_2\text{O})$ and $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$, is analysed, one can check that the species involved are discriminated by considering high (CO , H_2 and C_2H_4) and low (CH_4) temperature gas compounds. As already mentioned, temperature is a discriminant parameter among fumaroles but significant time-dependent

trends were not observed. Moreover, the above species participate in chemical reactions highly affected by redox conditions of the system (for example, $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, $4\text{H}_2 + 2\text{SO}_2 \rightleftharpoons \text{S}_2 + 4\text{H}_2\text{O}$ and $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$). In this framework the behaviour of the F27 fumarole is well discriminated from the others due to its higher temperature. If this fumarole is investigated in its future behaviour, changes in the redox conditions of the system can be clearly revealed, thus forecasting for important changes in the volcanic system.

The random behaviour of all the other chemical species analysed in this work appears to be related to the high variability of the log-ratios, thus giving a measure of their sensitivity to any change affecting the environment in time and/or space. This result indicates that their utility for monitoring parameters to be used in surveillance programmes is limited to the present state of the volcanic system.

Conclusions

Many systematic and random processes control the chemistry of gas discharges from active and quiescent volcanic areas, some of which may be defined poorly or understood inadequately. As a gas mixture is released by a magmatic body and moves toward the surface, complex chemical-physical reactions occur, according to variations in the level of volcanic activity, resulting in variable quantities of the non-magmatic/magmatic chemical species (Giggenbach 1996). Despite the complexity of volcanic system, fluid discharged at the surface may be modelled stochastically. Thus, experimental sampling designs are crucial since they will determine the independence of observations, thus informing about the best approach to data analysis. Moreover, if data are compositional, the choice of sample space has to be taken into account in order to build sound statistical models. In this experimental design seven fumaroles and sixteen variables were used to investigate the fumarolic field of Vulcano Island.

Investigation of geochemical parameters in log-ratio form has shown that gases from fumaroles F14, FNA and FZ have significant differences in $\ln(\text{SO}_2/\text{H}_2\text{O})$ and $\ln(\text{HCl}/\text{H}_2\text{O})$ in time and space; however, some mechanism able to homogenize the data in some periods of time independently of their spatial location for $\ln(\text{HCl}/\text{H}_2\text{O})$ occurs. This indicates that Vulcano has periodically experienced periods of time in which an intense fluid circulation was able to affect large portions of the crater, leading for a spatial diffusion of water-rock interaction processes. The $\text{H}_2\text{O}-\text{SO}_2-\text{HCl}$ subcomposition has been used to describe the relationships among the chemical species and

log-contrast principal component analysis permitted the research of equations similar to the Law of Mass Action. Following this path, chemical changes summarized by the log-contrasts have been analysed by considering their dependence from temperature, time and/or space. Log-contrast principal components are simple relationships able to take into account changes in important factors, such as the magmatic contribution, scrubbing, water–rock interactions, affecting the evolution of Vulcano. It is clear that in the investigated span of time, gas chemistry was highly variable. Causes of this variability are unclear but probably related to the high number of chemical–physical parameters affecting the chemical equilibria. Seismic activity 40 km offshore of Palermo, resulting in a $M = 5.8$ earthquake, abrupt outgassing off Panarea and volcanic eruptions at Stromboli in late 2002 through to summer 2003 suggest regional tectonic instability to which the changes in gas composition at Vulcano may be related (Biagi *et al.* 2004; Di Giovambattista & Tyupkin 2004; Caracausi *et al.* 2005; Calvari *et al.* 2005). The first and second log-contrast principal components account for such variation in gas composition of the fumaroles for Vulcano. Potentially, log-contrast equations can be used in the future to monitor further temporal changes. However, it may be that new data yield different log-contrasts that provide additional information to help model volcanic activity.

In addition, the statistical investigation reveals that the log-ratios $\ln(\text{H}_2/\text{H}_2\text{O})$, $\ln(\text{CO}/\text{H}_2\text{O})$, $\ln(\text{CH}_4/\text{H}_2\text{O})$ and $\ln(\text{C}_2\text{H}_4/\text{H}_2\text{O})$ are related to the sample site but no time dependency was revealed. It is concluded that temperature and redox conditions are a function of fumarole but temporal changes are essentially random.

Finally, for the other log-ratios $\ln(\text{CO}_2/\text{H}_2\text{O})$, $\ln(\text{H}_2\text{S}/\text{H}_2\text{O})$, $\ln(\text{S}/\text{H}_2\text{O})$, $\ln(\text{HF}/\text{H}_2\text{O})$, $\ln(\text{N}_2/\text{H}_2\text{O})$, $\ln(\text{O}_2/\text{H}_2\text{O})$, $\ln(\text{Ar}/\text{H}_2\text{O})$, $\ln(\text{Ne}/\text{H}_2\text{O})$, $\ln(\text{C}_2\text{H}_6/\text{H}_2\text{O})$ random variation over time and space is the fundamental pattern, thus compromising their use as monitoring tools in surveillance programmes.

The results obtained in this work allow one to conclude that the combined approach between geochemistry and statistics is a powerful tool for investigating complex volcanic systems evolving in time and space and where random variation is an important feature. In these situations, compositional data analysis appears to isolate variables responsible for significant changes, thus yielding parameters to be used in surveillance programmes for volcanic activity on a sound statistical base.

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References

- AITCHISON, J. 1982. The statistical analysis of compositional data (with discussion). *Journal of the Royal Statistical Society Series B*, **44** (2), 139–177.
- AITCHISON, J. 1983. Principal component analysis of compositional data. *Biometrika*, **70**, 57–65.
- AITCHISON, J. 1986. *The Statistical Analysis of Compositional Data*. Chapman & Hall, London.
- AITCHISON, J. 1999. Log-ratios and natural laws in compositional data analysis. *Mathematical Geology*, **24** (4), 365–379.
- BADALAMENTI, B., GUERRIERI, S., HAUSER, S., PARELLO, F. & VALENZA, M. 1988. Soil CO_2 output in the island of Vulcano during the period 1984–1988: surveillance of gas hazard and volcanic activity. *Rendiconti Societ  Italiana di Mineralogia e Petrologia*, **43**, 893–899.
- BARBERI, F., INNOCENTI, F., FERRARA, G., KELLER, J. & VILLARI, L. 1974. Evolution of Eolian arc volcanism (southern Thyrrenian sea). *Earth Planetary Science Letters*, **21**, 269–276.
- BAURBON, J., ALLARD, P. & TOUTAIN, J. 1990. Diffuse volcanic emissions of carbon dioxide from Vulcano Island, Italy. *Nature*, **344**, 51–53.
- BECCALUVA, L., GABBIANELLI, G., LUCCHINI, R., ROSSI, P. & SAVANELLI, C. 1985. Petrology and K/Ar ages of volcanics dredged from the Eolian seamount: implications for geodynamic evolution of the southern thyrrenian basin. *Earth Planetary Science Letters*, **74**, 187–200.
- BIAGI, P. F., PICCOLO, R., CASTELLANA, L. *ET AL.* 2004. Variations in a LF radio signal on the occasion of the recent seismic and volcanic activity in Southern Italy. *Tectonophysics*, **384**, 243–255.
- BOLOGNESI, L. & D'AMORE, F. 1993. Isotopic variation of the hydrothermal system on Vulcano Island, Italy. *Geochimica et Cosmochimica Acta*, **9**, 2069–2082.
- BUCCIANTI, A. & ESPOSITO, P. 2004. Insights into late quaternary calcareous nannoplankton assemblages under the theory of statistical analysis for compositional data. *Palaeogeography, Palaeoclimatology, Paleoecology*, **202**, 209–227.
- BUCCIANTI, A. & PAWLOWSKY-GLAHN, V. 2005. New perspectives on water chemistry and compositional data analysis. *Mathematical Geology*, **37** (7), 707–731.
- CALVARI, S., SPAMPINATO, L. & LODATO, L. 2005. The 5 April 2003 vulcanian paroxysmal explosion at Stromboli volcano (Italy) from field observations and thermal data. *Journal of Volcanology and Geothermal Research*, **149**, 160–175.
- CAPASSO, G., FAVARA, R., FRACOFONTE, S. & INGUAGGIATO, S. 1999. Chemical and isotopic variations in fumarolic discharge and thermal waters at Vulcano Island (Aeolian Islands, Italy) during 1996: evidence of resumed volcanic

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- CAPASSO, G., D'ALESSANDRO, W., FAVARA, R., INGUAGGIATO, S. & PARELLO, F. 2001. Interaction between the deep fluids and the shallow groundwaters on Vulcano Island (Italy). *Journal of Volcanology and Geothermal Research*, **108**, 187–198.
- CARACAUSI, A., DITTA, M., ITALIANO, F., LONGO, M., NUCCIO, P., PAONITA, A. & RIZZO, A. 2005. Changes in fluid geochemistry and physico-chemical conditions of geothermal systems caused by magmatic input: the recent abrupt outgassing off the island of Panarea (Aeolian Islands, Italy). *Geochimica et Cosmochimica Acta*, **69** (12), 3045–3059.
- CARAPEZZA, M., NUCCIO, P. M. & VALENZA, M. 1981. Genesis and evolution of the fumaroles of Vulcano (Aeolian Islands, Italy): a geochemical model. *Bulletin of Volcanology*, **44** (3), 547–563.
- CHIODINI, G., CIONI, R., FALSAPERLA, S., MONTALTO, A., GUIDI, A. & MARINI, L. 1992. Geo-chemical and seismological investigations at Vulcano (Aeolian Islands) during 1978–1989. *Journal of Geophysical Research*, **97**, 11025–11032.
- CHIODINI, G., CIONI, R. & MARINI, L. 1993. Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance. *Applied Geochemistry*, **8**, 357–371.
- CHIODINI, G., CIONI, R., MARINI, L. & PANICHI, C. 1995. Origin of the fumaroles fluids of Vulcano Island, Italy and implications for volcanic surveillance. *Bulletin of Volcanology*, **57**, 99–110.
- CIONI, R. & D'AMORE, F. 1984. A genetic model for the crater fumaroles of Vulcano Island (Sicily, Italy). *Geothermics*, **13** (4), 375–384.
- CORTECCI, G., FERRARA, G. & DINELLI, E., 1996. Isotopic time-variations and variety of sources for sulfur in fumaroles at Vulcano Island, Aeolian Archipelago, Italy. *Acta Vulcanologica*, **8**, 147–160.
- CORTECCI, G., DINELLI, E., BOLOGNESI, L., BOSCHETTI, T. & FERRARA, G. 2001. Chemical and isotopic composition of water and dissolved sulfate from shallow wells on Vulcano Island, Aeolian Archipelago, Italy. *Geothermics*, **30**, 69–91.
- DEASTIS, G., LA VOLPE, L., PECCERILLO, A. & CIVETTA, L. 1997. Volcanological and petrological evolution of Vulcano island (Aeolian arc, Southern Tyrrhenian Sea). *Journal of Geophysical Research*, **102**, 8021–8051.
- DI GIOVAMBATTISTA, R. & TYUPKIN, Y. S. 2004. Seismicity patterns before the m05.8 2003, Palermo (Italy) earthquake: seismic quiescence and accelerating seismicity. *Tectonophysics*, **384**, 243–255.
- DI LIBERTO, V., NUCCIO, P. M. & PAONITA, A. 2002. Genesis of chlorine and sulphur in fumarolic emissions at Vulcano Island (Italy): assessment of pH and redox conditions in the hydrothermal system. *Journal of Volcanology and Geothermal Research*, **116**, 137–150.
- EGOZCUE, J., PAWLOWSKY-GLAHN, V., MATEU-FIGUERAS, G. & BARCELO-VIDAL, C. 2003. Isometric log-ratio transformations for compositional data analysis. *Mathematical Geology*, **35** (3), 279–300.
- FOUQUÉ, F. 1856. Sur les phénomènes éruptifs de l'Italie méridionale. *Comptes Rendus de la Société Géologique de France, Paris*, **XLI**, 565–567.
- FREPOLI, A., SELVAGGI, C., CHIARABBA, G. & AMATO, A. 1996. State of stress in the southern tyrrhenian subduction zone from fault-plane solutions. *Geophysical Journal International*, **125**, 879–891.
- GIGGENBACH, W. F. 1996. Chemical composition of volcanic gases. In: SCARPA, R. & TILLING, R. I. (eds) *Monitoring and Mitigation of Volcano Hazards*. Springer-Verlag, Berlin-Heidelberg, Germany, 221–256.
- LEEMAN, W., TONARINI, S., PENNISI, M. & FERRARA, G. 2005. Boron isotopic variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: implications for evolution of volcanic fluids. *Geochimica et Cosmochimica Acta*, **69** (1), 143–163.
- MARTINI, M. 1980. Geochemical survey on the phreatic waters of Vulcano (Aeolian Islands, Italy). *Bulletin of Volcanology*, **43** (1), 265–274.
- MARTINI, M. 1983. Variations in surface manifestation at Vulcano (Aeolian Islands, Italy) as a possible evidence of deep processes. *Bulletin of Volcanology*, **46** (1), 83–86.
- MARTINI, M. 1993. Water and fire: Vulcano island from 1977 to 1991. *Geochemical Journal*, **27**, 297–303.
- MARTINI, M. 1996. Chemical characters of the gaseous phase in different stages of volcanism: precursors and volcanic activity. In: SCARPA, R. & TILLING, R. I. (eds) *Monitoring and Mitigation of Volcanic Hazard*. Springer Verlag, Berlin Heidelberg, Germany, 200–219.
- MARTINI, M. & TONANI, F. 1970. *Rilevamento idrogeologico di Vulcano*. Rapporti I e IA, CNR n. 6900544, Palermo, Italy.
- MAZOR, E., CIONI, R., CORAZZA, E. ET AL. 1988. Evolution of fumarolic gases – boundary conditions set by measured parameters: case study at Vulcano, Italy. *Bulletin of Volcanology*, **50**, 71–85.
- MINISALE, A. 1992. Isotopic composition of natural thermal discharges on Vulcano Island, southern Italy. *Journal of Hydrology*, **139**, 15–25.
- MONTALTO, A. 1996. Signs of potential renewal of eruptive activity at La Fossa (Vulcano, Aeolian Islands). *Bulletin of Volcanology*, **57**, 483–492.
- MONTEGROSSI, G., TASSI, F., VASELLI, O., BUCCIANI, A. & GAROFALO, K. 2001. Sulfur species in volcanic gases. *Analytical Chemistry*, **73** (15), 3709–3715.
- PANICHI, C. & NOTO, P. 1992. Isotopic and chemical composition of water, steam and gas samples of the natural manifestations of the island of Vulcano Aeolian Arc, Italy. *Acta Vulcanologica*, **2**, 297–312.
- PAWLOWSKY-GLAHN, V. & BUCCIANI, A. 2002. Visualization and modelling of sub-populations of compositional data: statistical methods illustrated by means of geochemical data from fumarolic

- fluids. *International Journal of Earth Sciences*, **91**, 357–368.
- PAWLOWSKY-GLAHN, V. & EGOZCUE, J. 2001. Geometric approach to statistical analysis on the simplex. *Stochastic Environmental Research and Risk Assessment*, **15** (5), 384–398.
- PIRILLO, L., VASELLI, O. & TASSI, F. 2002. Studio della distribuzione areale e delle variazioni stagionali dei composti gassosi nelle fumarole dell'Isola di Vulcano (Italia meridionale). *82 SIMP Congress, Cosenza, Italy*, 242–243.
- REYMENT, R. A. & SAVAZZI, E. 1999. *Aspects of Multivariate Statistical Analysis in Geology*, Elsevier, Amsterdam.
- SAINTE-CLARE DEVILLE, C. 1856. Sur les phenomenes eruptifs du Vesuve et de l'Italie Meridionale. *Comptes rendus de la Societe Geologique de France, Paris*, **XLI**, 606–610.
- SHINOHARA, H. & MATSUO, S. 1986. Results of analyses on fumarolic gases from F1 and F5 fumaroles of Vulcano, Italy. *Geothermics*, **15** (2), 211–215.
- SICARDI, L. 1940. Il recente ciclo dell'attivita fumarola dell'isola di Vulcano. *Bulletin of Volcanology*, **7**, 85–139.
- SYMONDS, R., GERLACH, T. & REED, M. 2001. Magmatic gas scrubbing: implications for volcano monitoring. *Journal of Volcanology and Geothermal Research*, **108**, 303–341.
- VASELLI, O., TASSI, F., CAPACCIONI, B., TEDESCO, D., BELLUCCI, F. & PIRILLO, L. 2003. Le manifestazioni fumaroliche e le acque di falda dell'Isola di Vulcano nel periodo Novembre 2002–Marzo 2003. *Geolitalia 2003, IV Forum FIST, Italy*, 440.
- VON EYNATTEN, H., PAWLOWSKY-GLAHN, V. & EGOZCUE, J. 2002. Understanding perturbation on the simplex: a simple method to better visualise and interpret compositional data in ternary diagrams. *Mathematical Geology*, **34** (3), 249–275.
- VON EYNATTEN, H., BARCELO-VIDAL, C. & PAWLOWSKY-GLAHN, V. 2003a. Composition and discrimination of sandstone: a statistical evaluation of different analytical methods. *Journal of Sedimentary Research*, **73** (1), 47–57.
- VON EYNATTEN, H., BARCELO-VIDAL, C. & PAWLOWSKY-GLAHN, V. 2003b. Modelling compositional changes: the example of chemical weathering of granitoid rocks. *Mathematical Geology*, **35** (3), 231–251.