

Statistical evidences of cyclic changes in volcanic gas chemistry composition by inverse modelling

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Abstract

The identification of compositional changes in fumarolic gases of active and quiescent volcanoes is one of the most important targets in monitoring programs. From a general point of view, many systematic (often cyclic) and random processes control the chemistry of gas discharges, making difficult to produce a convincing mathematical-statistical modelling.

Changes in the chemical composition of volcanic gases sampled at Vulcano Island (Aeolian Arc, Sicily, Italy) from eight different fumaroles located in the northern sector of the summit crater (La Fossa) have been analysed by considering their dependence from time in the period 2000-2007. Each intermediate chemical composition has been considered as potentially derived from the contribution of the two temporal extremes represented by the 2000 and 2007 samples, respectively, by using inverse modelling methodologies for compositional data. Data pertaining to fumaroles F5 and F27, located on the rim and in the inner part of La Fossa crater, respectively, have been used to achieve the proposed aim. The statistical approach has allowed us to highlight the presence of random and not random fluctuations, features useful to understand how the volcanic system works, opening new perspectives in sampling strategies and in the evaluation of the natural risk related to a quiescent volcano.

1. Introduction

Volcanic emanations consist of solid and liquid particles and gases. Usually the gas phase primarily consists of water vapour (H_2O), CO_2 , SO_2 , HCl , HF and other gas compounds in smaller amounts (e.g. H_2 , CO , H_2S , noble gases, hydrocarbons), including many different metals (Delmelle and Stix, 2000). Although the tectonic setting and the chemical-physical parameters characterizing magma degassing (e.g. solubility of the species in the melts) control the chemical composition of high-temperature volcanic gases, most compositional variations of the fumarolic discharges appear to be related to processes involving, at relatively shallow depth, hydrothermal fluids and/or meteoric water affecting the magmatic system. When hot gases interact with shallow aquifers, the result is a fumarolic discharge containing little information on the initial magmatic gas composition, being the high-temperature gas species, i.e. SO_2 and HCl , strongly affected by secondary processes (gas-water-rock interaction). Sulfur dioxide may indeed interact with liquid water in the hydrothermal system, thus modifying the pristine $\text{H}_2\text{S}/\text{SO}_2$ ratio. In some cases this reaction yields elemental sulfur, whose deposition and re-volatilisation affects the concentration of sulfur compounds in the gas phase. Similarly, HCl may be dissolved in aquifers, being its solubility in water relatively high, especially at $\text{pH} > 3$. Magmatic gas scrubbing and the implications of this phenomenon for volcanic surveillance have experimentally and theoretically been investigated by Symonds et al. (2001). Scrubbing includes dissolution into the aqueous phase (hydrolysis), and formation of precipitates (sulfur, sulfides, fluorides, sulfates) from gas-water or gas-water-rock interactions. Accordingly, scrubbing phenomena have a greater impact on gases (SO_2 , HCl , HF) that produce strong acids in water with respect to those that form weaker acids (CO_2 , H_2S). Consequently CO_2 (the most important carbon gas compound) may be the main species to monitor when scrubbing is present, being the least soluble in magmatic melts and exclusively released from its parent magma by the time it reaches the surface, unless contribution from other sources are not involved (e.g. sedimentary and organic). Since in volcanic systems there are no major sources and sinks for CO_2 , it can be considered a conservative component, unaffected by secondary processes, similar to noble gases, or non-reactive gases (Tassi et al., 2007). In other words, any variation in the relative proportions of a species with respect to CO_2 are likely to reflect the occurrence of processes affecting that species rather than CO_2 (Giggenbach, 1996).

The origin of short-term (hours) variations in the concentration of sulfur species (SO_2 , H_2S , and S^0) of crater fumaroles discharging at different temperatures (up to 410°C) from five volcanic systems was investigated by Montegrossi et al. (2008). The results of the study suggest that short-term natural (self-induced) fluctuations of the sulfur species can be generated by the dissipation mechanisms of the entropy excess of the discharging system that gives rise to dissipative structures (Prigogine, 1969), a phenomenon that should be taken into serious account for geochemical monitoring purposes. However, these authors have focused the attention only on the sulfur species as an independent subsystem within the whole composition, as suggested by the results of a biplot-graphical analysis followed by a log-contrast one. The present work considers a wider chemical composition of a volcanic gas mixture (CO_2 , HCl , HF , SO_2 , H_2S , S , H_2O , N_2 , CH_4 , Ar , Ne , H_2 , He and CO) and extends the investigation on a relatively large temporal arc (ca. 7 years) during which significant chemical changes have occurred. Only chemical species such as O_2 , C_2H_4 and C_6H_6 , characterised by the presence of numerous data below the detection limit, were excluded. Compositional variations were traced by using inverse modelling procedures for a dataset where the chemistry of two crater fumaroles (F5 and F27), collected in October 2000 and January 2007, respectively, was chosen as temporal end-members.

2. Geological and geochemical background

Vulcano Island is the southernmost and the third largest (ca. 22 km^2) of the seven major islands of the volcanic calc-alkaline arc that form the Aeolian Archipelago (Sicily, Italy). The central part of the island is characterised by La Fossa active cone, whose last eruption occurred in 1888-1890, and developed in the last 6 kyr through the homonymous caldera (Fig. 1). From 1890 up to now La Fossa has remained in a fumarolic stage despite transient periods of “volcanic unrest” (Montalto, 1996). After the 1888-1890 eruption two main episodes of increasing fumarolic activity have indeed been recorded: 1913-1923 (Sicardi, 1941) and 1978-1989 (Chiodini et al., 1995), so that the fumarolic field and the hydrothermally altered areas have significantly enlarged (Boyce et al., 2007) (Fig. 1).

The gas discharges of the Vulcano magmatic-hydrothermal system, mainly localized in the inner part and on the northern edges of La Fossa crater, are characterized by medium-to-high outlet temperature (up to 700°C in late 1980s) and redox conditions dominated by the $\text{SO}_2/\text{H}_2\text{S}$ gas buffer (Chiodini et al., 1993). Fumarolic activity fed by a well-developed hydrothermal system is present at the beach area along the north-eastern seashore, and characterized by lower outlet temperatures ($T \leq 100^\circ\text{C}$) and more reducing conditions (Capaccioni et al., 2001).

The first chemical data for fumarolic discharges were reported by Sainte-Clare Deville (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. On the whole, the magmatic fluids are thought to originate from the degassing of the relatively shallow ($\leq 4\text{ km}$) magmatic system that feeds La Fossa crater (Bolognesi and D'Amore, 1993; Chiodini et al., 1995; Martini, 1996; Montalto, 1996; Capasso et al., 1997; Gioncada et al., 1998; Fulignati et al., 1998; Capasso et al., 1999; 2001; Di Liberto et al., 2002; Aiuppa et al., 2006; Bucciatti et al., 2006; Peccerillo et al., 2006).

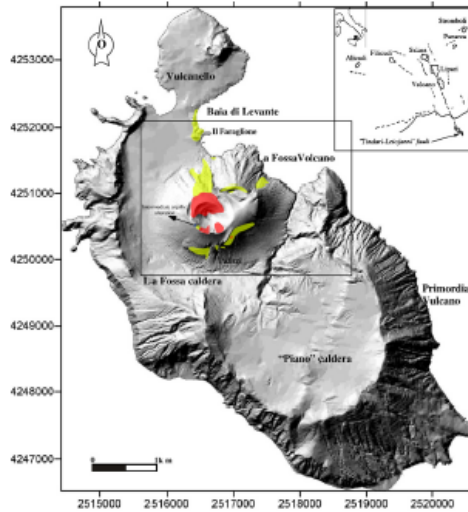


Figure 1. DEM (Digital Elevation Model) of the Island of Vulcano and areal distribution (red area = silicic alteration, yellow area = advanced argillitic alteration) of the hydrothermal facies (after Boyce et al., 2007).

The great variability of the Vulcano fumarole field, in terms of outlet temperature and gas chemistry, 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: i) crater rim and ii) outer and iii) inner fumaroles, the latter two being geographically referred to the crater rim itself. The *crater rim* gas discharges vary widely in temperatures (100-450 °C). Steam is the main component (up to 98×10^4 $\mu\text{mol/mol}$) but high temperature gases (e.g. SO_2 , HCl , HF , CO) are important. The *outer* fumaroles are mainly located along fractures that extend outwards from the rim and can reach temperatures up to 100 °C; their composition is generally H_2O -dominated and show relatively high concentrations of H_2S , N_2 and H_2 . The *inner* fumaroles display outlet temperatures similar to those of the *outer* gas discharges but a higher chemical variability is recorded. The wide-ranging behaviour of the fumarolic field of La Fossa crater suggests that only the monitoring of an elevated number of fumarolic vents over time can be able to give information on the whole system. Consequently, eight 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), three from the rim itself (FNA, F5, F11) and three from the inner part of the crater rim (F14, F27, F202). In this paper only the fumaroles F5 and F27 have been analysed by considering the presence of data for the whole period of time 2000-2007.

3. Statistical analysis

3.1 Investigating the simplex geometry

The statistical analysis of compositional data had an independent status when Aitchison (1986) introduced the additive-logratio (alr) and centered-logratio (clr) transformations, as well as an appropriate distance in the simplex, the sample space of compositional data without zero parts. These transformations from the simplex into multidimensional real space exhibit important properties as invariance under scale group of transformations, sub-compositional consistency, correspondence of the group of translations in multidimensional real space with the group of perturbations in the simplex. Statistical models were successfully developed in most cases, as can be seen in the monograph by Aitchison (1986) and later applications (Barcelò-Vidal, et al., 2001; Billheimer et al., 2001; Pawlowsky-Glahn and Egozcue, 2001, 2002; von Eynatten et al., 2002; Egozcue et al., 2003; Buccianti and Pawlowsky-Glahn, 2005). From a geometrical point of view, the space occupied by compositional data is called *simplex of D parts*, S^D (D is the number of variables = parts) and includes all positive real vectors adding up to a constant that for simplicity we take as the unit. Accordingly, absolute values of components in a composition are meaningless unless they are compared by ratios with other components. We use the notation S^D , where the superscript is the number of parts of the composition. The D -part simplex is defined as:

$$S^D = \left\{ \mathbf{x} = (x_1, x_2, \dots, x_D), x_i > 0, i = 1, \dots, D; \sum_{i=1}^D x_i = k \right\}$$

where k is an arbitrary positive constant, e.g. 1 if measurements are performed in parts per 1 or 100 if they are in percentages or 10^6 .

In the simplex geometry the basic operation of *perturbation* (Aitchison, 1986, p. 42) has revealed a great importance. Perturbation is computed by multiplying compositions component by component and, afterwards, dividing each component by the sum of all of them to attain unit sum. This last normalization is called *closure* and does not affect the ratios between components. The underlying reason for the importance of perturbation is that it plays a role in the simplex precisely analogous to displacement or translation in the real space; it is a mechanism for recording change. For example, if a D -part composition \mathbf{x} changes through whatever process to a D -part composition \mathbf{y} , the change can be ascribed to a perturbation \mathbf{p} . The *perturbation* operation, defined for any two compositions $\mathbf{x}, \mathbf{y} \in S^D$, is given by:

$$\mathbf{x} \oplus \mathbf{y} = C[x_1 y_1, x_2 y_2, \dots, x_D y_D],$$

where $C[.]$ is the closure operator (i.e. each component is divided by the sum of all the components and then multiplied by k , so that the resulting row vector is in S^D).

There is a second operation in the simplex, *powering*, i.e. the analogue of scalar multiplication in the real space. Powering a composition by a real constant consists of raising each component to the constant and then applying closure to the result. For $\mathbf{x} \in S^D$ and $\alpha \in \mathbf{R}$ powering is given by:

$$\alpha \otimes \mathbf{x} = C[x_1^\alpha, x_2^\alpha, \dots, x_D^\alpha].$$

The operations define a $D - 1$ dimensional vector or linear space structure on S^D (Pawlowsky-Glahn and Egozcue, 2002). The structure can be extended to produce a metric vector space by the introduction of the *simplicial metric or distance* ΔS defined by Aitchison (1983) as:

$$\Delta S(\mathbf{x}, \mathbf{y}) = \left[\sum_{i=1}^D \left\{ \ln \frac{x_i}{g(\mathbf{x})} - \ln \frac{y_i}{g(\mathbf{y})} \right\}^2 \right]^{1/2}$$

where $g(\cdot)$ denotes the geometric mean of the components of the enclosed vector. This distance plays a fundamental role in inverse modelling procedures for compositional data (Aitchison and Bacon-Shone, 1999). Inverse methods concern the presence of source compositions, say, y_1, \dots, y_c , from which a generic observed composition x arises as a convex linear combination $x = \pi_1 y_1 + \dots + \pi_c y_c$. The values of π_i , the non-negative mixing proportions, can be evaluated following different paths. In any case the distance between the real data and the estimated one has to be minimised during an iterative process. When the Aitchison's distance (Aitchison, 1983) is considered, the nature of compositional data is taken into account in the simplicial metric. This approach has been followed in our analysis.

3.2 Random and not random fluctuations

In order to verify the presence of natural fluctuations in the chemical composition of volcanic gases, as already testified for the sulphur sub-composition (Montegrossi et al., 2008), an inverse modelling procedure has been applied on the variables CO_2 , HCl , HF , SO_2 , H_2S , S , H_2O , N_2 , CH_4 , Ar , Ne , H_2 , He and CO , by solving a linear least squares problem with non-negativity constraints and distances as required for compositional data (convex linear mixing problem, Aitchison and Bacon-Shone, 1999). Variables such as O_2 , C_2H_4 and C_6H_6 have been excluded in this phase of the analysis due to the presence of several data below the detection limit. Since samples have been collected from October 2000 up to January 2007, these two temporal extremes were chosen as temporal *end-members*. The first part of the investigation has involved the F5 fumarole, located on the crater rim, whose chemical composition of 2000 and 2007 samples is reported in Table 1.

If the perturbation operation is applied with the aim to evaluate the compositional difference that characterise the two compositions, it is possible to conclude that most important difference between the 2007 to 2000 chemistry is attributable to HCl since it shows a relative increase corresponding to a perturbation effect of 0.23, followed by SO_2 (0.15), H_2 (0.14) and He (0.13), considering that 1 is the sum of the perturbation effects and a fraction of 1 is assigned to each variable. Temperature appears to show a non-stationary behaviour with respect to the mean value in time as it significantly increases from 231 to 264 °C (Runs test, $p < 0.05$; Hallin and Puri, 1995). The inverse modelling results, given by the percentage contributions of each extreme, are reported in Fig. 2 as a function of the sampling months. If the presence of random or not random fluctuations in the relative contribution of the two temporal extremes has to be valued, statistical analysis would be applied on the log-ratio between the two percentage contributions (contribution of 2007 rationed to those of 2000).

F5 fumarole μmol/mol	Sample of 2000 October	Sample of 2007 January
<i>CO₂</i>	107,637	46,271
<i>HCl</i>	257.2	1016
<i>HF</i>	29.52	36.04
<i>SO₂</i>	952.5	2,367
<i>H₂S</i>	5168	1119
<i>S</i>	0.838	0.103
<i>H₂O</i>	885,215	948,457
<i>N₂</i>	604.3	429.6
<i>CH₄</i>	0.032	0.018
<i>Ar</i>	2.460	0.330
<i>Ne</i>	0.0014	0.0002
<i>H₂</i>	128.6	302.58
<i>He</i>	0.408	0.926
<i>CO</i>	0.073	0.103

Table1. Composition of the samples collected in 2000 and 2007, representing the temporal extremes for F5 fumarole. Data are in μmol/mol.

The application of Kolmogorov-Smirnov test indicates that the log-ratio follows the normal distribution ($p > 0.05$) and the Runs test, with respect to the mean value, reveals that the data are not randomly distributed ($p < 0.05$). Fluctuations between the chemical composition of 2000 and 2007 for F5 fumarole appear to be non-stationary in time (Fig. 3). In this framework, temperature follows the normal model (KS-test, $p > 0.05$), also showing a non-randomness of the values around the mean (Runs test, $p < 0.05$). Finally the correlation between temperature and log-ratio values is equal to $r = +0.67$ (non parametric correlation).

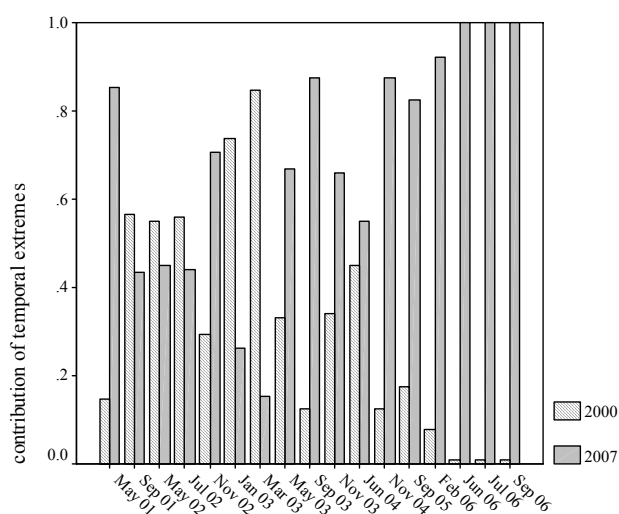


Figure 2. Contribution in time of the two extreme temporal compositions sampled in 2000 and 2007 in reconstructing each intermediate sample for F5 fumarole.

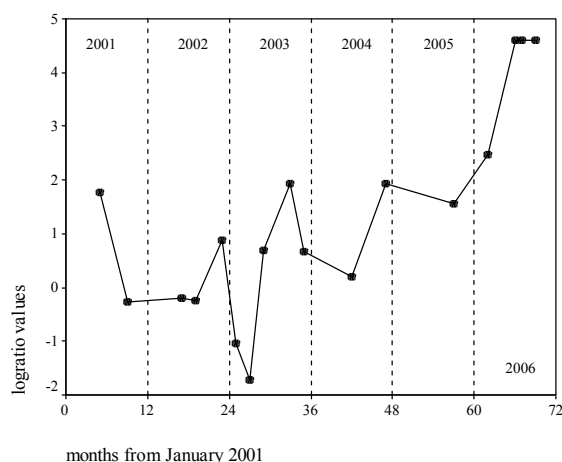


Figure 3. Time dependence of the logratio values given by the contribution of 2007 chemistry rationed with respect to the 2000 one, F5 fumarole.

The second step of investigation has involved fumarole F27 located in the inner part of the crater rim. Data related to the chemistry of the relative temporal extremes used in the inverse modelling procedure are reported in Table 2.

F27 fumarole μmol/mol	Sample of 2000 October	Sample of 2007 January
<i>CO₂</i>	62,512	31,018
<i>HCl</i>	2,443	497.1
<i>HF</i>	18.95	9.31
<i>SO₂</i>	2101	1777
<i>H₂S</i>	725.9	146.9
<i>S</i>	< d.l.	0.117
<i>H₂O</i>	930,372	966,174
<i>N₂</i>	1,486	356
<i>CH₄</i>	0.016	0.005
<i>Ar</i>	1.147	0.434
<i>Ne</i>	0.0007	0.0003
<i>H₂</i>	337.2	20.6
<i>He</i>	0.240	0.500
<i>CO</i>	2.252	0.209

Table 2. Composition of the samples collected in 2000 and 2007, representing the temporal extremes for F27 fumarole. Data are in μmol/mol.

The application of the perturbation operator allows us to evidence the variables that mainly contribute to the chemical changes from 2000 to 2007 samples in fumarole F27. HF is the variable that shows the most important changes, with a decreasing corresponding to a perturbation of about 0.41, followed by CO (0.14) and HCl and SO₂ (both 0.1). This four variables decrease their contribution from 2000 to 2007. In the other cases the variables are subjected to a minor perturbation effect.

The results of the inverse modelling procedure for fumarole F27 are reported in Fig. 4. The Kolmogorov-Smirnov test indicates that normality can be accepted for the log-ratio between the two percentages contributions (contribution of 2007 rationed to those of 2000). By applying the Runs test the presence of random fluctuations of the log-ratio values around the mean (Fig. 5) is observed, evidencing a different result if compared with fumarole F5. Temperature values are not stationary with respect to the mean value and significantly decrease from 2000 (398.3 °C) to 2007 (336 °C) (Runs test, $p < 0.05$).

Finally, the negative correlation between the log-ratio values and temperature is significant ($p < 0.05$), though low ($r = -0.58$, non-parametric correlation coefficient).

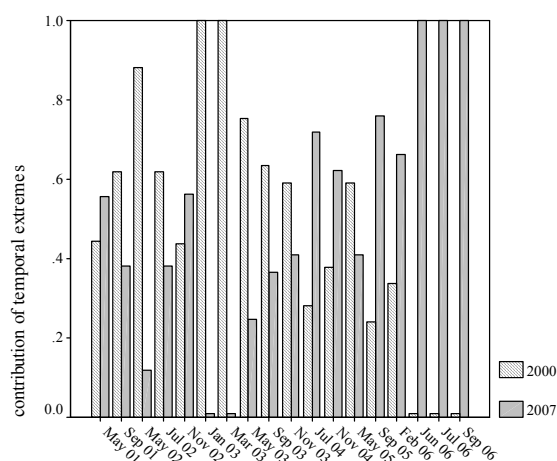


Figure 4. Contribution in time of the two extreme temporal compositions sampled in 2000 and 2007 in reconstructing each intermediate sample, F27 fumarole.

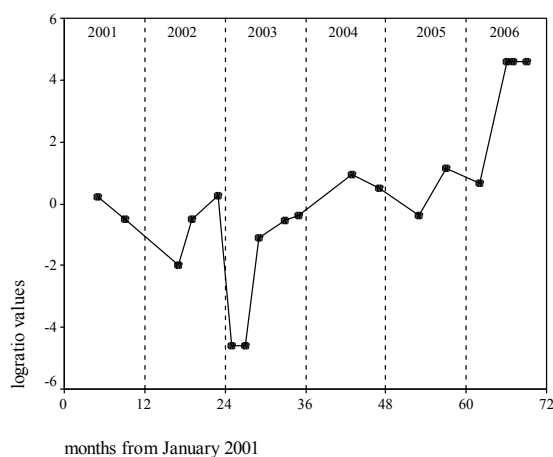


Figure 5. Time dependence of the log-ratio values given by the contribution of 2007 chemistry rationed with respect to the 2000 one, F27 fumarole.

Discussion and conclusions

As mentioned, the temperature of the crater rim fumarole F5 has a non stationary behaviour with respect to the mean value in time varying from 231 to 264 °C from 2000 to 2007. The fluctuations of the contribution in time of the chemical compositions of 2000 and 2007 in reconstructing each intermediate sample (percentage contribution of 2007 rationed to those of 2000) also appear to be non-stationary in time and consequently correlated with temperature. The most important chemical differences between the 2000 and 2007 samples are related to a significant increase in HCl, SO₂, H₂ and He, which could be related to higher temperature and/or lower dependence on scrubbing phenomena, possibly due to decreasing interactions with the shallow environment. The outlet temperature of the fumarole F27 is not stationary with respect to the mean value and decreases from 2000 (398.3 °C) to 2007 (336 °C). The fluctuations of the contribution in time of the chemical compositions of 2000 and 2007 in reconstructing each intermediate sample (percentage contribution of 2007 rationed to those of 2000) appear to be random in time and consequently not well correlated with temperature. This behaviour agrees with the variations of chemical compositions that record a significant decrease from 2000 to 2007 samples of HF, followed by CO, HCl and SO₂, likely related to either a change of the contribution of the deep-seated fluids and/or an increase of scrubbing phenomena.

The physical and chemical decoupling of F5 and F27 fumaroles can be visualised in Fig. 6 where the log-ratoned contributions obtained by inverse modelling are plotted together. The variation range of F27 is higher than F5 where extreme negative values (contribution of the 2007 chemistry much lower than that of 2000) are not found. It is evident that the fumarole F27 registers more extreme phenomena in subsequent time intervals. In other words, it is characterised by a minor cumulative capacity of the changes direction. This behaviour may be responsible for the random fluctuations in time. From this point of view, the system described by F27 fumarole appears to be more instable in taking into account the directions of chemical changes when compared to those of F5. To be noticed here is that the time

dependence of the log-ratio values of the two fumaroles is similar in September and July 2001 and 2006 and in June 2006. The most important differences have been recorded in March 2003 and in other rainy months.

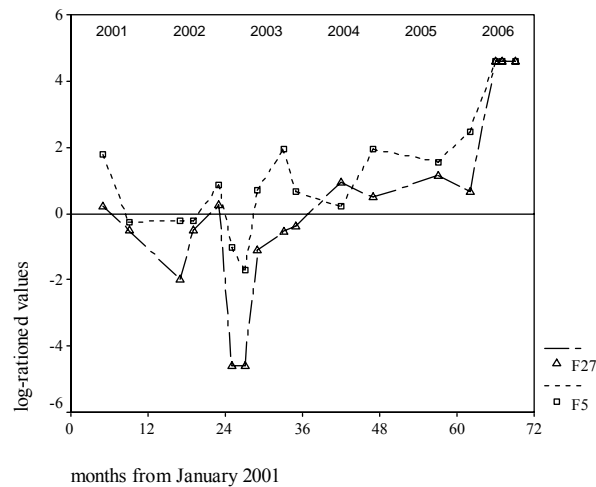


Figure 6. Comparison between the log-ratios contributions (2007/2000) for fumaroles F5 and F27.

These results suggest that in summer time the quantity of meteoric water affecting the discharging vents is reduced, and, consequently the chemical features of the two fumaroles, mostly depending on contribution of deep fluids, show a similar behaviour in time. On the contrary, rainy seasons are able to enhance the influence of the scrubbing processes as meteoric water infiltrates through the fractured fumarolized areas, producing the different temporal pattern of the two discharging systems. Therefore, the different location of the two fumaroles may play a fundamental role for determining fumarolic chemistry (Fig. 7).



Figure 7. Spatial position of the fumaroles F5 and F27 in the Vulcano fumarolic field. The position of all the other sampling sites is also reported.

The F5 fumarole, positioned at the border of the fumarolic field, is indeed more exposed to rainwater circulating at shallow depth than the F27 fumarole, located at the centre of a zone characterized by the presence of high-temperature gas discharges. However, contributions due to self-sealing processes and changing in fracturation due to micro-seismic activity controlling fumaroles migration cannot be ruled out. These processes can be responsible for variability but also for the probable homogenization of the system as for example is occurring in recent time (Fig. 6).

The result obtained in this work implies that the sampling strategy in a complex fumarolic field such as that of La Fossa crater has to be conveniently planned by considering the different chemical-physical aspects of the gas discharges and their position with respect to area where they are preferentially emitted. The statistical approach presented in this work has pointed out a new perspective for evaluating the chemical changes in a relatively long periodical (though discontinuous) sampling that may be applied in terms of both understanding the primary and secondary mechanisms affecting the composition of a fumarolic vent and correlating these variations to volcanic surveillance programs.

References

- 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., Bacon-Shone J., 1999. Convec linear combinations of compositions. *Biometrika*, 86, 351–364.
- Aiuppa A., Federico C., Giudice G., Guerrieri S. & Valenza M., 2006. Hydrothermal buffering of the SO₂/H₂S ratio in volcanic gases: evidence from La Fossa Crater fumarolic field, Vulcano Island. *Geoph. Res. Lett.*, 33, L21315.
- Billheimer D, Guttorp P, Fagan W., 2001. Statistical interpretation of species composition. *Jour. Am. Stat. Assoc.* 96(456):1205–1214
- Barcelò-Vidal C., Martín-Fernández J. A. & Pawlowsky-Glahn V., 2001. Mathematical foundations of compositional data analysis, in Ross G. (Ed.), *Proceedings of IAMG'01—The sixth annual conference of the International Association for Mathematical Geology*, CD-ROM, 20 p.
- Bolognesi, L. & D'Amore, F., 1993. Isotopic variation of the hydrothermal system on Vulcano Island, Italy. *Geochim. Cosmochim. Acta* 57, 2069–2082.
- Boyce A.J., Fulignati P., Sbrana A. & Fallick A., 2007. Fluids in early stage hydrothermal alteration of high sulfidation epithermal system: a view from the Vulcano active hydrothermal system (Aeolian Island, Italy). *J. Volcanol. Geoth. Res.*, 166, 76–90.
- Buccianti A. & Pawlowsky-Glahn V., 2005. New perspectives on water chemistry and compositional data analysis. *Mathem. Geol.*, 37 (7), 707–731.
- Buccianti A., Tassi F. & Vaselli O., 2006. Compositional changes in a fumarolic field, Vulcano Island, Italy: a statistical case study. *Geological Society, London, Special Publications* 264, 67–77.
- Capaccioni, B., Tassi, F., Vaselli, O., 2001. Organic and inorganic geochemistry of low temperature gas manifestations at the Baia di Levante beach, Vulcano Island (Aeolian Archipelago, Southern Italy). *J. Volcanol. Geotherm. Res.*, 108, 173–185.
- Capasso, G., Favara, R. & Inguaggiato, S., 1997. Chemical features and isotopic composition of gaseous manifestations on Vulcano Island, Aeolian Islands, Italy: an interpretative model of fluid circulation. *Geochim. Cosmochim. Acta* 61, 3425–3440.
- 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 activity. *J. Volcanol. and Geoth. Res.*, 88, 167–175.
- 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). *Jour. Volcanol. and Geoth. Res.*, 108, 187–198.
- Chiodini G., Cioni R. & Marini L., 1993. Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance. *Appl. Geochem.* 8, 357–371.
- Chiodini G., Cioni R., Marini L. & Panichi, C., 1995. Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance. *Bull. Volcanol.* 57, 99–110.
- Delmelle P. & Stix J., 2000. Volcanic Gases. In: *Encyclopedia of volcanoes*. Academic, New York, pp 803–815.
- 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. *Jour. Volcanol. and Geoth. Res.*, 116, 137–150.
- Egozcue J. J., Pawlowsky-Glahn V., Mateu-Figueras G. & Barcelò-Vidal C., 2003. Isometric logratio transformations for compositional data analysis. *Mathem. Geol.*, 35 (3), 279–300.
- Fouqué F. 1856. Sur le phenomenes eruptifs de l'Italie meridionale. *Comptes Rendus de la Societe Geologique de France*, Paris, XLI, 565–567.
- Fulignati P., Gioncada A. & Sbrana, A., 1998. Geologic model of the magmatic-hydrothermal system of Vulcano (Aeolian Island Italy). *Mineral. Petrol.* 62, 195–222.
- 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.
- Gioncada A., Clocchiatti R., Sbrana A., Bottazzi P., Massar, D. & Ottolini L., 1998. A study of melt inclusions at Vulcano (Aeolian islands, Italy): insight on the primitive magmas and on the volcanic feeding system. *Bull. Volcanol.* 60, 286–306.
- Hallin M. & Puri M.L., 1995. A multivariate Wald-Wolfowitz Rank Test against serial dependence. *The Canadian Journal of Statistics*, 23(1), 55–65.
- 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.
- Montalto A., 1996. Signs of potential renewal of eruptive activity at La Fossa (Vulcano, Aeolian Islands). *Bull. Volcanol.* 57, 483–492.

- Montegrossi G., Tassi F., Vaselli O., Minissale A., Buccianti A., 2008. Natural fluctuations of sulfur species (SO_2 , H_2S , $\text{S}_8(0)$) in volcanic fumaroles. *Jour. of Non-equilib. Thermodynamics*, in press.
- Pawlowsky-Glahn V. & Egozcue J. J., 2001. Geometric approach to statistical analysis on the simplex. *Stochastic Environmental Research and Risk Assessment*, 15 (5), 384–398.
- Pawlowsky-Glahn V. & Egozcue J. J., 2002, BLU estimators and compositional data: *Mathem. Geol.*, v. 34, no. 3, p. 259–274.
- Peccherillo A., Frezzotti M.L., De Astis G. & Ventura G., 2006. Modeling the magma plumbing system of Vulcano (Aeolian Islands, Italy) by integrated fluid-inclusion geobarometry, petrology and geophysics. *Geol. Soc. of Am.*, 34, 1, 17–20.
- Pirillo L. 2003. Le manifestazioni fumaroliche e le acque di falda dell'Isola di Vulcano nel periodo Novembre 2002–Marzo 2003. *GeoItalia 2003*, IV Forum FIST, Italy, 440.
- 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.
- Prigogine, I. 1969. Structure, dissipation and life. In: "Theoretical Physics and Biology", M. Mariolis (ed.), North Holland Publish., Amsterdam, The Nederland, 212 pp.
- 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.
- Sicardi, L., 1941. Il recente ciclo dell'attività fumarolica dell'isola di Vulcano, *Bull. Volcanol.* 7, 85–140.
- Symonds, R., Gerlach, T. & Reed, M. 2001. Magmatic gas scrubbing: implications for volcano monitoring. *J Volcanol. Geoth. Res*, 108, 303–341.
- Tassi, F., Vaselli, O., Capaccioni, B., Montegrossi, G., Barahona, F. & Caprai, A. 2007. Scrubbing processes and thermodynamic reactions regulating the composition of light hydrocarbons in natural gas discharges: an example from Ahuachapan and Berlin geothermal fields (Salvador). *Geochem. Geophys. Geosyst.*, 8, Q05008, doi:10.1029/2006GC001487.
- Vaselli O., Tassi F., Capaccioni B., Tedesco D., Bellucci, F. & 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. *Mathem. Geol.*, 34 (3), 249–275.