



**HAL**  
open science

## Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995

Maddalena Pennisi, Marie-Françoise Le Cloarec

► **To cite this version:**

Maddalena Pennisi, Marie-Françoise Le Cloarec. Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995. *Journal of Geophysical Research: Solid Earth*, 1998, 103 (B3), pp.5061-5066. 10.1029/97JB03011 . hal-03119683

**HAL Id: hal-03119683**

**<https://hal.science/hal-03119683v1>**

Submitted on 25 Jan 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995

Maddalena Pennisi

Istituto di Geocronologia e Geochimica Isotopica, Consiglio Nazionale delle Ricerche, Pisa, Italy

Marie-Françoise Le Cloarec

Centre des Faibles Radioactivités, Centre National de la Recherche Scientifique - Commissariat à l'Énergie Atomique Gif sur Yvette, France

**Abstract.** This study investigates data on the Cl, F, and S concentrations of plume-filter samples collected between 1992 and 1995 from Mount Etna. The samples were collected during eruptive and noneruptive activity and show fairly constant Cl/F ratios but wide variation in the Cl/S ratios. The determination of the Cl/F ratio (between 5 and 14) allows an estimate of F degassing to be derived that ranges from 10 to 30% of the initial F content of the magma. The variation in the Cl/S ratio fits an empirical two-stage degassing model where gas with high Cl/S ratio is discharged during quiescent degassing and gas with low Cl/S ratios is discharged during eruptive degassing. The typical permanent degassing occurs from a depth at which chlorine exsolution exceeds sulfur exsolution ( $Cl/S > 1$ ). The opposite of this behavior is observed during eruptive periods when significant sulfur degassing occurs because magma degasses at near atmospheric pressure ( $Cl/S \sim 0.1$ ). The Cl/S ratio in the plume, characterizing the type of degassing, has the potential to be a useful geochemical tool for monitoring the volcano.

### 1. Introduction

Mount Etna discharges a permanent volcanic plume consisting of hot magmatic gases which issues from four open conduits at the summit.  $SO_2$ , HCl, and HF are described as the dominant sulfur and halogen species in the Mount Etna plume with much smaller amounts of particulate chlorides, fluorides, and sulfates [Faivre-Pierret *et al.*, 1980; Andres *et al.*, 1993], although thermodynamic calculations indicate that NaCl and KCl are the main halogen components [Le Guern, 1988]. Varekamp *et al.* [1986] reported an enrichment in Al and Fe sulfates, which they explained as being due to the low Cl/F ratio of the plume (5) controlling the vapor transport of Al and rare earth elements and possibly other elements (e.g., Si) against Na, K, and metals (enriched in Cl-rich plumes). The discharge of heavy metals from the volcano to the atmosphere was estimated for the 1976 eruption [Buat-Menard and Arnold, 1978] and for the "quite activity" during July 1987 [Andres *et al.*, 1993]. From the study of the 1983 eruption, potassium particulate content in the plume was suggested as helpful in characterizing the volcanic activity [Quisefit *et al.*, 1988]. An extensive series of data has been acquired for the short-lived aerosols ( $^{210}Pb$ ,  $^{210}Bi$ ,  $^{210}Po$ ) of the  $^{238}U$  family; their activities in the plume during both eruptive and noneruptive periods have been shown to be a tool for characterizing the type of activity occurring at Mount Etna [Lambert *et al.*, 1986; Le Cloarec *et al.*, 1988].

Measurements of the Cl/S ratio in gas discharges from other volcanoes show that generally the ratio decreases prior to

eruption [Stoiber and Rose, 1970; Menyailov, 1975] due to the outgassing of less degassed magma. A few measurements of the Cl/S ratio in Mount Etna's plume during the eruptive activities have been reported [Buat-Menard and Arnold, 1978; Faivre-Pierret *et al.*, 1980] and data on the Cl/S ratio during quiescent activity were reported by Andres *et al.*, [1993] and Francis *et al.* [1995]. The aim of this paper is to investigate the Cl/F and Cl/S ratios with respect to the changing volcanic activity. The S (measured as  $SO_2$ ), Cl, and F contents were investigated in the Bocca Nuova, Voragine, and Sud-Est plumes (Figure 1) during the 1991-1993 eruption, one of the most prolonged and volumetrically significant eruptions observed over the last 300 years at Mount Etna [Calvari *et al.*, 1994], then during the post-eruptive phase in 1993, a few months after the end of the eruption, during quiescent degassing in 1994, and finally during Strombolian activity in 1995.

### 2. Sampling and Analyses

The plumes of the summit craters were sampled as close as possible to the rims. Wind conditions were taken into account in order to avoid mixed plumes. In 1992 the degassing occurred from two cones located on the craters floor about 250 and 130 m from the rim at Voragine and Bocca Nuova, respectively. Explosions often occurred with no visible extrusion of lava. The Sud-Est plume, enriched in water vapor, discharged quietly from two main vents located a few tens of meters from the collection point. During 1993 and 1994 the same field conditions were observed with the exception that the intracrateric cone of Voragine was partly destroyed and that only the northern vent was active at the Sud-Est crater.

Copyright 1998 by the American Geophysical Union.

Paper number 97JB03011.  
0148-0227/98/97JB-03011\$09.00

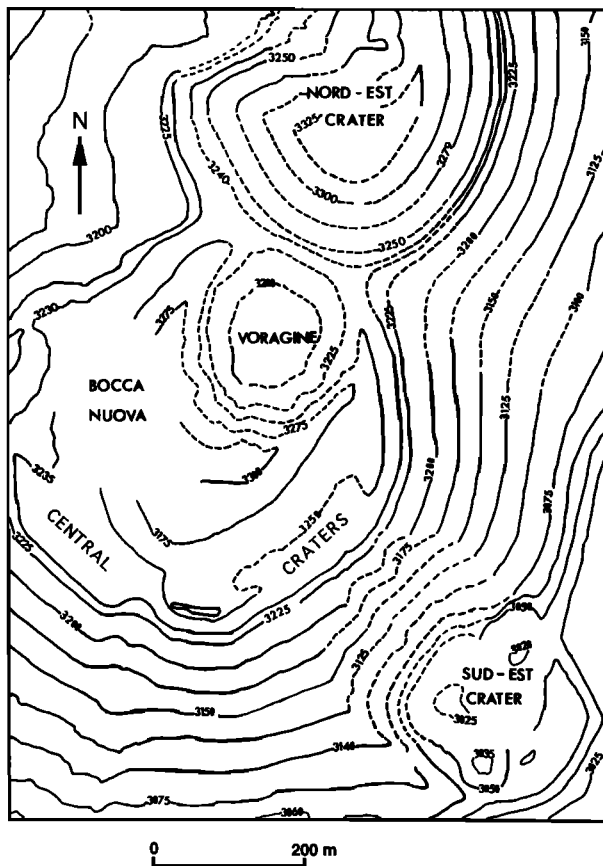


Figure 1. Location map of the summit area [after Murray *et al.*, 1981].

Lower  $\text{SO}_2$  fluxes were measured during 1993 (about 1500–2000 t/d) than during 1994 (3000 t/d; T. Caltabiano, personal communication, 1994). During 1995, ash emissions and explosions were recorded in July and August at Bocca Nuova crater (Coltelli M., personal communication, 1995), before plume sampling in September.

The sampling device consists of two filter holders connected to a small pump attached to a 2 m long pole. Each filter holder consists of two Millipore cellulose filters (in series), impregnated following the techniques described by Faivre-Pierret [1983]. During sampling, the filters are held far from the soil to minimize soil contamination or are kept off the rim to avoid any contribution from the rim fumaroles. The flow rate (calibrated at 2400 m) was 4 L/min. Saturation levels are 2, 1, and 9 mg on the filter for HCl, HF, and  $\text{SO}_2$ , respectively. In the laboratory, both filters of each holder are washed and then analyzed for Cl<sup>-</sup> by ion chromatography, for F<sup>-</sup> by specific electrode, and for  $\text{SO}_2$  by colorimetry. The analytical error is about 10%. On each filter holder, the trapping efficiency on the first filter ranges between 90 and 95%, as indicated by the Cl, F, and  $\text{SO}_2$  amounts measured on the second filter (4% Cl, 8% F, and 10%  $\text{SO}_2$ ). Particles can not be excluded on the filters but are considered negligible with respect to gas contribution [Faivre-Pierret *et al.*, 1980; Andres *et al.*, 1993].

### 3. Results

Concentrations of Cl, F, and  $\text{SO}_2$  (expressed as  $\text{mg}/\text{m}^3$ ) are reported in Table 1. All analyzed plumes show a positive

correlation between Cl and F (Figure 2). The Cl/F ratios (weight ratios) inferred from the slope of the lines are 14, 6, and 3 at Bocca Nuova (BN), Voragine (V), and Sud-Est (SE), respectively, suggesting crater-specific Cl/F ratios. While at BN the Cl/F ratio is clearly higher than at V and SE, there are not enough measurements to ensure that the ratio at the SE crater is really different from that observed in the V plume.

The Cl/F ratios range between 7.5 and 19.4 at Bocca Nuova (except for the ratio of 5.1 measured during 1994), between 3.6 and 12.7 at Sud-Est, and between 4.2 and 7.8 at Voragine. It is worth noting that during 1995 the Cl and F data for the SE plume approach the line characterizing the BN plume (Figure 2). Thus, although there are very few SE

Table 1. Cl, F, and  $\text{SO}_2$  Contents in the Plume of Mount Etna During 1992, 1993, 1994, and 1995

Summit Craters	Date	Cl	F	$\text{SO}_2$
Bocca Nuova	Jan. 16, 1992	0.15	n.d.	1.67
Voragine	Jan. 16, 1992	0.88	n.d.	9.22
Bocca Nuova	June 24, 1992	1.39	0.07	2.80
Sud-Est	June 24, 1992	6.51	n.d.	9.30
Bocca Nuova	June 26, 1992	5.41	0.48	32.00
Bocca Nuova	Oct. 25, 1992	6.14	0.60	67.00
Bocca Nuova	Oct. 25, 1992	4.42	n.d.	49.00
Bocca Nuova	Oct. 25, 1992	3.46	0.46	37.00
Bocca Nuova	June 7, 1993	16.55	n.d.	16.40
Voragine	June 7, 1993	28.73	5.27	14.40
Bocca Nuova	June 8, 1993	22.57	1.43	14.40
Bocca Nuova	June 9, 1993	23.38	1.40	18.10
Voragine	June 9, 1993	21.95	3.55	20.50
Voragine	June 9, 1993	27.27	4.91	18.93
Bocca Nuova	June 10, 1993	9.16	n.d.	18.51
Bocca Nuova	June 10, 1993	50.18	n.d.	30.41
Voragine	June 10, 1993	15.55	n.d.	15.19
Sud-Est	June 10, 1993	48.00	11.27	23.14
Sud-Est	June 10, 1993	54.68	14.73	27.58
Bocca Nuova	June 11, 1993	44.73	3.68	9.96
Voragine	June 11, 1993	22.09	3.41	6.66
Sud-Est	June 11, 1993	59.05	16.23	n.d.
Bocca Nuova	June 12, 1993	37.82	2.18	33.98
Voragine	June 12, 1993	17.05	2.18	12.55
Bocca Nuova	June 14, 1993	22.45	1.70	21.40
Voragine	June 15, 1993	21.09	3.91	9.00
Bocca Nuova	June 17, 1993	18.55	n.d.	30.44
Voragine	June 17, 1993	11.55	2.00	n.d.
Voragine	June 17, 1993	11.73	n.d.	6.85
Bocca Nuova	June 18, 1993	16.36	n.d.	7.96
Voragine	June 18, 1994	6.24	1.33	25.63
Bocca Nuova	June 20, 1994	5.40	1.06	14.33
Voragine	June 20, 1994	17.20	2.22	48.10
Voragine	June 21, 1994	9.75	1.97	12.54
Bocca Nuova	June 22, 1994	4.51	n.d.	13.61
Bocca Nuova	June 22, 1994	3.52	n.d.	10.59
Voragine	June 22, 1994	3.37	0.77	7.42
Voragine	June 22, 1994	9.58	1.78	9.08
Voragine	June 23, 1994	10.60	2.15	24.83
Voragine	June 23, 1994	12.37	2.34	15.39
Sud-Est	June 23, 1994	21.25	4.48	29.78
Sud-Est	June 23, 1994	n.d.	4.75	66.57
Bocca Nuova	Sept. 15, 1995	5.36	0.46	21.10
Bocca Nuova	Sept. 16, 1995	5.34	0.61	18.70
Sud-Est	Sept. 16, 1995	12.52	1.05	32.20
Sud-Est	Sept. 16, 1995	12.88	1.02	43.50

Concentrations in  $\text{mg}/\text{m}^3$ ; n.d., not detected.

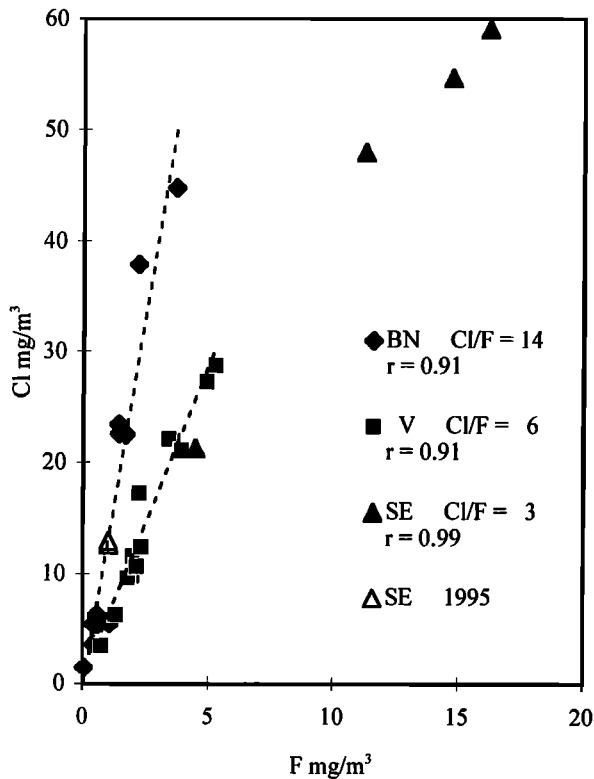


Figure 2. Variations in time of Cl and F contents in the plumes of the summit craters.

samples, the large variability of their 1995 Cl/F ratios when compared to their 1993 and 1994 Cl/F ratios is probably controlled by activity rather than by input from the crater rim fumaroles. It was suggested previously that low temperature fumaroles can increase the Cl content thereby leading to high Cl/F ratios [Faivre-Pierret et al., 1980; Miller et al., 1990]. This could explain the daily variation at the Cl/F ratio that was sometimes recorded; the acquisition of a consistent set of data could help in detecting unreliable samples. Moreover, it seems from the F/S and Cl/S ratios in 1995 that the significant variability is mainly due to F depletion than to Cl increase. According to the above considerations we suggest that the available data on the Cl/F ratio are not sufficient to allow any detection of new magma entering the shallow system [Miller et al., 1990]. We suggest instead that the Cl/F ratios between 5 (V+SE) and 14 (BN) should be considered as characteristic features of the volcano for further applications. The ratios measured in the period 1992-1995 are in agreement with previous analyses of Cl/F = 9 for gas samples collected at the hornitos of the 1983 eruption [Le Guern, 1988], and with  $4 < Cl/F < 9$  in the summit plume during 1978, 1981, and 1987 activities [Faivre-Pierret et al., 1980; Varekamp et al., 1986; Andres et al., 1993]. More generally, it appears that Cl/F ratios between 4 and 13 are fairly typical for high-temperature volcanic gases [Symond et al., 1994].

The Cl/S ratio in the separated plumes of the summit craters indicates that the plumes of Bocca Nuova and Voragine, and probably that of Sud-Est are characterized by similar Cl/S signatures during a given period of activity (Figure 3). Significant differences are shown on the Cl/S ratio of the plume, which varied by a factor 50 over the period of investigation, for the three craters or even for a single crater

(Bocca Nuova). Changes in the Cl/S ratio occurred from one year of sampling to another. Typically, the Cl/S ratio was about 0.3 during the 1992 eruption and increased to about 3-4 during 1993 by the end of the eruption. Intermediate values of 0.9 and 0.6 are recorded during 1994 and 1995, respectively. As a first approximation, low Cl/S ratios (0.2-0.6) seem consistent with eruptive or strombolian degassing, while higher Cl/S ratios characterize the plume during quiescent activity.

#### 4. Discussion

##### 4.1. Chlorine and Fluorine Degassing at Mount Etna

The Cl/F ratios measured at Mount Etna plume during 1992-1995 display a small range of variation, less than one order of magnitude. At present, we have no explanation for the different Cl/F ratios measured for each crater. In particular, they can not be explained by selective contributions from a crust formed on the magma column during low activity [Le Guern, 1988], as shown by the fairly constant Cl/F ratios at BN during both eruptive and noneruptive periods. The positive correlation between Cl and F observed at BN and V suggests that the magma is the unique source for both elements. This observation might also suggest that the exsolution of these halogens is governed by the same physical conditions, such as temperature and/or pressure for example.

From the analyses of melt inclusions in olivine phenocrysts the Cl/F ratio in Mount Etna primitive basalts is about 3.6 [Metrich et al., 1993]. Based on this value and noting that the plume Cl/F ratio is between 5 and 14, the

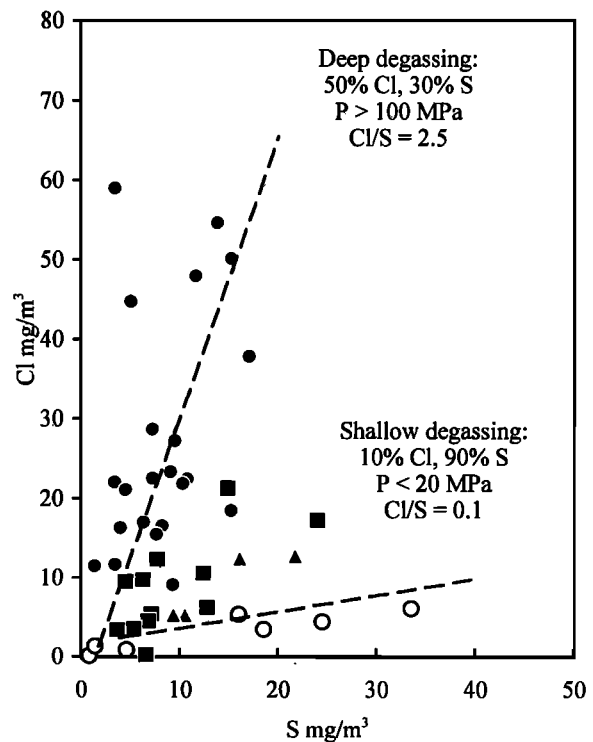


Figure 3. Comparison of the Cl and S data measured in the summit craters plumes with the hypothetical chemical composition of the fluid phase at  $P > 100$  MPa, and at  $P < 20$  MPa following a model based on the whole rock and fluid inclusions [Metrich and Clocchiatti, 1989]. Open circle, 1992; solid circle, 1993; square, 1994; solid triangle, 1995.

partition coefficient of Cl into the gas phase (partition coefficient =  $Cl_{\text{gas}}/Cl_{\text{magma}}$ ) should be about 1.4 to 3.9 times that of F. Given that in present-day hawaiitic lavas from Mount Etna the degassing of Cl has been quantified as around 40-50% [Metrich and Clocchiatti, 1989], we estimate that between 10 and 30% of the initial magmatic F is degassed. This new result supports the general idea of a poor degassing of F from magmas but is not in agreement with the negligible degassing of F compared to that of Cl reported for Mount Etna [Metrich, 1990]. We believe that Metrich's data are not sufficient to investigate F behavior because of the small number of F analyses (6) when compared to the number of Cl measurements (26).

It should also be recognized that the effect of melt and fluid composition, pressure, and temperature on Cl and F solubility in melts are still not well characterized for the range of magma compositions encountered in nature [Carrol and Webster, 1994, and references therein]. Empirical studies show that volcanoes degass different amounts of Cl and F, each according to the physical and chemical characteristics of the degassing magma. For instance, based on the strong correlation between Cl and other nonvolatile elements, the degassing of Cl from basalts from Iceland is considered to be less than 10% [Sigvaldason and Oskarsson, 1976]. Another example is drawn from the study of glass inclusions and quenched glass in products from the various stages of eruption [Thordarson and Self, 1996]. This work shows that 66% of total Cl and in 37% of total F degassed from the Roza member of the Columbia River Basalt Group.

Considering both the richness of Etnean tholeiites in chlorine (compared to Mid Atlantic Ridge basalts [Metrich, 1990]) and the huge degassing activity of the volcano, the quantification of the Cl (about 50%) and F (15-30%) degassing suggests Mount Etna's plume is a significant natural source of halogen to the atmosphere.

#### 4.2. Chlorine and Sulfur Degassing at Mount Etna

The Cl/S variation at Mount Etna over the period 1992-1995 may be explained as follows. During 1992 the volcanic plume was sustained by full or "deep" degassing of convecting and erupting magma. This eruption was the largest at Mount Etna over the past three centuries [Calvari et al., 1994] and was associated with a huge release of  $SO_2$  [Bruno et al., 1994]. This left a residual degassed magma (for sulfur at least) with a high Cl/S ratio in the conduit system which then sustained a variable Cl-rich plume during the June 1993 post-eruptive phase. As new magma entered the system, as also indicated by a  $SO_2$  flux increase (T. Caltabiano, personal communication, 1993), "steady" gas release was restored giving average Cl/S ratio of 0.9-0.6 in 1994-1995. This model follows the "classical" interpretation [e.g. Stoiber and Rose, 1970], where the Cl/S ratio increases with the degree of degassing of the magma because the solubility of Cl in the magma exceeds that of S. According to this model the Cl/S variation is mainly determined by the evolution of sulfur degassing. As a consequence, changing activity from the degassing of erupting magma to the degassing of S-exhausted magma should account for a huge variation in the  $SO_2$  flux but produces a fairly constant HCl flux (during both the eruptive and the residual-magma degassing).

However, data for the HCl flux calculated from the Cl/S ratios in the plume and  $SO_2$  fluxes during the same period

[Pennisi et al., 1997] are not consistent with the model considered above. During the eruptive period (1992) a 10,000 t/d flux was measured for  $SO_2$ , with the corresponding HCl flux estimated at 1000 t/d. During the post-eruptive period, in June 1993, the  $SO_2$  flux was 1500-2000 t/d, while HCl flux ranged from 3000 to 4000 t/d. High HCl fluxes (3800 t/d) are also estimated for low  $SO_2$  fluxes (1120 t/d) and high Cl/S ratios (3.4, measured at BN) during a "quiet activity" in July 1987 [Andres et al., 1993]. The threefold to fourfold increase in the HCl flux from eruptive to quiescent degassing is consistent with an increase in the Cl exsolution from the magma rather than the simple evolution of sulfur degassing from one stage of activity to the other. Although a simple increase in the volume of degassed magma could account for the increased Cl flux, this seems unlikely because the higher Cl fluxes occurred during post-eruptive activity.

#### 4.3. Two-Stage Degassing Model

We attempt to explain these results using a two-stage degassing model deduced from mineralogy and from the S and Cl content in melt inclusions and in the whole rock of the 1763, 1865, and 1929 eruptions of Mount Etna [Metrich and Clocchiatti, 1989]. At the basalt-hawaiite transition (crystallization of olivine Fo74, salite, and plagioclase) about 50% of chlorine and 30% of sulfur are extracted from the system. This degassing occurs at pressures greater than 100 MPa and is consistent with the permanent outgassing present at Mount Etna. At this pressure, no evidence exists of gas saturation [Clocchiatti et al., 1992; Metrich and Clocchiatti, 1996]. In order to explain the low S content of the whole rock (about 100 ppm), these authors suggested a second degassing stage, which occurs during eruptions (or at least during a degassing close to the surface at  $P < 20$  MPa) and accounts for the degassing of 90% of S. The release of Cl during this phase is limited. Although there is no clear evidence yet for the pressure dependence of HCl solubility in basalts, this empirical observation is consistent with experimental studies on felsic magmas showing a decrease of Cl solubility in the melt with increasing pressure [Kilinc and Burnham, 1972; Anderson, 1974; Shinohara et al., 1989]. In order to calculate the Cl/S ratio in the fluid phase that is issued during the two main observed degassing stages, we will assume in the following discussion an initial content of 1560 ppm of S and 2300 ppm of Cl, as measured in melt inclusions of the 1991-1993 eruption [Armenti et al., 1994]. These concentrations fall in the ranges 1500-2400 and 1600-2400 ppm generally observed in olivine inclusions for S and Cl, respectively [Metrich and Clocchiatti, 1989]. During the "first degassing stage" the degassing of 50% Cl and 30% S from a deep magma yields a fluid characterized by a Cl/S ratio equal to 2.5 and a depleted magma containing about 1100 ppm S and 1150 ppm Cl. During the second degassing stage the degassing of 90% S and 10% Cl will produce a fluid phase with Cl/S = 0.1. The two Cl/S ratios of 2.5 and 0.1 are considered the current limits of the Cl/S ratio in the magma degassing at Mount Etna. Figure 3 shows the comparison between the rock-degassing model and the data measured in the plume: the Cl/S ratios in the plume fall inside the range assigned by the rock model to the gas; all samples from the 1992 eruption approach the "shallow degassing line", while the 1993 samples fit quite well with the "permanent degassing line". Intermediate behavior is shown for the 1994 and the 1995 samples.

In the light of the two-stage degassing model some revision of previous plume studies [Faivre-Pierret *et al.*, 1980] is suggested. The Cl/S ratio of about 0.3 measured in June 1978 belongs to a period of almost continuous eruptive activity, which occurred from April to June, and in August and November [Tanguy and Kieffer, 1993]. This result is in agreement with our data on the eruptive plume, but it is interpreted by Faivre-Pierret *et al.* [1980] as indicative of "deep degassing" on the basis of the theoretical laws of gas solubilities and on empirical observations of the Cl/S ratio in volcanic gases [Menyailov, 1975]. In the light of our study the characterization of the degassing as "deep" or "shallow" inferred by the Cl/S ratio has been reversed: the "deep" degassing yields an enrichment in chlorine with respect to sulfur. The "shallow degassing" during eruptions occurs close to atmospheric pressure and yields an enrichment in sulfur with respect to chlorine.

## 5. Conclusion

The Cl, F, and S contents measured in the plume of Mount Etna during eruptive and noneruptive activities show that the F degassing at Mount Etna ranges from 10 to 30% of the initial F content in the magma. The Cl/S ratios measured during eruptive activity (average Cl/S = 0.3) differ strongly from the Cl/S ratios measured one month after the end of the eruption (average Cl/S = 4). The variations of the Cl/S ratio observed in the plume correlate significantly with an empirical degassing model derived from the study of the melt inclusions and of the rocks of Mount Etna. Following this model, the plume chemistry, characterized by the Cl/S ratio, can help in distinguishing "deep degassing" ( $P > 100$  MPa) from shallow degassing ( $P \approx 0.1$  MPa). An anomalously shallow asthenosphere is considered responsible for the 20-30 km deep subcrustal reservoir at Mount Etna [Tanguy *et al.*, 1997]. Convective movements within this mantle lens lead to continuous degassing, even without migration of magma [D'Alessandro *et al.*, 1997]. According to Badalamenti *et al.* [1994], changes in magma pressure within the deep reservoir can be detected by variable CO<sub>2</sub> flux in the peripheral areas of the volcano. We suggest that both deep and shallow degassing can be detected by the plume chemistry. The Cl/S ratio is close to 3 when a nonequilibrium rise of bubbles from the deep reservoir dominates over the degassing of the strongly degassed liquid, filling (with low convective movements) the upper level of the volcano. Drop in pressure caused both by magma pressure and tectonic movements triggers vesiculation and drives the deep-degassed magma toward shallow level. At this stage, the Cl/S ratio rises to 0.2 in the plume, leading to a shallow degassing signature dominating over the deep one. The 1991-1993 eruption of Mount Etna provided an important opportunity to test the model, as the plume signature changed in relation with injection of new magma in 1992 and its termination in June 1993. During the following noneruptive period a decrease of the Cl/S ratio was recorded from Cl/S = 0.9 in June 1994 to Cl/S = 0.6 in September 1995. Data obtained by Fourier transform infrared spectroscopy during September 1994 [Francis *et al.*, 1995] report Cl/S ratios ranging between 0.6 and 0.7; these data confirm our June 1994 results and concur in supporting the Cl/S ratio as an indicator for the gentle recharging of the system that occurs from June 1994 until the

Strombolian activity which began in July 1995. This conclusion is in contrast with other studies suggesting that gas-chemistry changes may not precede ascending magma [Gerlach, 1986].

The 1994 data show that uprising magma might be detected by changes in the Cl/S ratio but still might not precede an eruption. This process has already been recognized at Mount Etna [Lambert *et al.*, 1986] and can account for the observed decreases in the Cl/S ratio during quiescent periods not followed by an eruption. It is still unknown how common this feature is and for this reason the monitoring of the feeding system during noneruptive periods is suggested as the main focus for forthcoming studies of the plume of Mount Etna.

**Acknowledgments.** This work was supported by the program "CEE Environment". We thank N. Metrich, B. Symonds, J.C. Varekamp and two anonymous reviewers for their help in improving the manuscript. *Contribution CFR 1977.*

## References

- Anderson, A.T., Chlorine, sulphur and water in magmas and oceans, *Geol. Soc. Am. Bull.*, **85**, 1485-1492, 1974.
- Andres, R.J., P.R. Kyle, and R.L. Chuan, Sulfur dioxide, particle and elemental emissions from Mount Etna, Italy during July 1987, *Geol. Rund.*, **82**, 687-695, 1993.
- Armienti, P., R. Clocchiatti, M. D'Orazio, F. Innocenti, R. Petri, M. Pompilio, S. Tonarini, and L. Villari, The long-standing 1991-1993 Mount Etna eruption: Petrography and geochemistry of lavas, *Acta Vulcanol.*, **4**, 15-28, 1994.
- Badalamenti, B., G. Capasso, M.L. Carapezza, W. D'Alessandro, F. Di Gangi, I.S. Diliberto, S. Giammanco, S. Gurrieri, F. Parello, and M. Valenza, Soil gases investigations during the 1991-1993 eruption, *Acta Vulcanol.*, **4**, 134-141, 1994.
- Bruno, N., T. Caltabiano, M.F. Grasso, M. Porto, and R. Romano, SO<sub>2</sub> flux from Mt. Etna volcano during the 1991-1993 eruption: Correlation and considerations, *Acta Vulcanol.*, **4**, 143-147, 1994.
- Buat-Menard, P., and M. Arnold, The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano, *Geophys. Res. Lett.*, **5**, 245-248, 1978.
- Calvari, S., M. Coltelli, M. Pompilio, and V. Scribano, 1991-1993 Mount Etna eruption: Chronology and lava flow field evolution, *Acta Vulcanol.*, **4**, 1-14, 1994.
- Carroll, M.R., and J.D. Webster, Solubilities of sulfur, noble gases, nitrogen, chlorine and fluorine in magmas, in *Volatiles in Magmas*, *Rev. Mineral.*, vol.30, edited by M. R. Carroll and J. R. Holloway, pp. 231-280, Mineral. Soc. of Am., Washington, D.C., 1994.
- Clocchiatti, R., J. Weiz, M. Moshab, and J.C. Tanguy, Coexistence de "verres" alcalins et tholéitiques saturés en CO<sub>2</sub> dans les olivines des hyaloclastites d'Aci Castello (Etna, Sicile, Italie): Arguments en faveur d'un manteau anormal et d'un réservoir profond, *Acta Vulcanol.*, **2**, 161-173, 1992.
- D'Alessandro, W., S. Giammanco, F. Parello, and M. Valenza, CO<sub>2</sub> output and  $\delta^{13}\text{C}$  (CO<sub>2</sub>) from Mount Etna as indicators of degassing of shallow asthenosphere, *Bull. Vulcanol.*, **58**, 455-458, 1997.
- Faivre-Pierret, R., SO<sub>2</sub>, HCl, and HF detection and dosing in the volcanic gas phase, in *Forecasting volcanic events*, edited by H. Tazieff and J.C. Sabroux, pp. 399-408, Elsevier, New York, 1983.
- Faivre-Pierret, R., D. Martin, and J.C. Sabroux, Contribution des sondes aérologiques motorisées à l'étude de la physico-chimie des panaches volcaniques, *Bull. Vulcanol.*, **43-3**, 473-485, 1980.
- Francis, P., A. Maciejewski, C. Oppenheimer, C. Chaffin, and T. Caltabiano, SO<sub>2</sub>:HCl ratios in the plumes from Mt. Etna and Vulcano determined by Fourier transform spectroscopy, *Geophys. Res. Lett.*, **22**, 1717-1720, 1995.
- Gerlach, T.M., Exsolution of H<sub>2</sub>O, CO<sub>2</sub>, and S during eruptive episodes at Kilauea volcano, Hawaii, *J. Geophys. Res.*, **91**, 12177-12185, 1986.
- Kilinc, I.A., and C.W. Burnham, Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kbar, *Econ. Geol.*, **67**, 231-235, 1972.
- Lambert, G., M.F. Le Cloarec, B. Arduin, and J.C. Le Rouley, Volcanic emission of radionuclides and magma dynamics, *Earth Planet. Sci. Lett.*, **76**, 185-192, 1986.

- Le Cloarec, M.F., and M. Pennisi, Degassing processes at Mount Etna during the period 1983-1994: Radionuclides constraints, paper presented at IAVCEI General Assembly, Int. Assoc. of Volcanol. and Chem. of the Earth's Inter., Puerto Vallarta, Mexico, Jan. 19-24, 1997.
- Le Cloarec, M.F., M. Pennisi, B. Ardouin, J.C. Le Rouley, and G. Lambert, Relationship between gases and volcanic activity of Mount Etna in 1986, *J. Geophys. Res.*, **93**, 4477-4484, 1988.
- Le Guern, F., Ecoulement gazeux réactifs à hautes températures, mesures et modélisation, thèse de Doctorat d'Etat, 314 pp., Univ. Paris VII, 1988.
- Menyailov, I.A., Prediction of eruptions using changes in composition of volcanic gases, *Bull. Volcanol.*, **39**, 112-125, 1975.
- Metrich, N., Chlorine and fluorine in tholeiitic and alkaline lavas of Etna (Sicily), *J. Volcanol. Geotherm. Res.*, **40**, 133-148, 1990.
- Metrich, N., and R. Clocchiatti, Melt inclusion investigation of the volatile behaviour in historic alkali basaltic magmas of Etna, *Bull. Volcanol.*, **51**, 185-198, 1989.
- Metrich, N., and R. Clocchiatti, Sulfur abundance and its speciation in oxidized alkaline melts, *Geochim. Cosmochim. Acta*, **60**, 4151-4160, 1996.
- Metrich, N., R. Clocchiatti, M. Mosbah, and M. Chaussidon, The 1989-1990 activity of Etna: Magma mingling and ascent of H<sub>2</sub>O-Cl-S-rich basaltic magma: Evidence for melt inclusions, *J. Volcanol. Geotherm. Res.*, **59**, 131-144, 1993.
- Miller, T.L., W.H. Zoller, B.M. Crowe, and D.L. Finnegan, Variations in trace metal and halogen ratios in magmatic gases through an eruptive cycle of the Pu'u O'o Vent, Kilauea, Hawaii: July-August 1985, *J. Geophys. Res.*, **95**, 12607-12615, 1990.
- Murray J.B., C.R.J. Kilburn, T.J. Sanderson, S. Benazon, C. Crooks, and A. Pullen, Sommità dell'Etna, Ordnance Survey, Southampton, England, 1981.
- Pennisi M., T. Caltabiano, and M.F. Le Cloarec, Chlorine, fluorine and sulfur emissions from Mt. Etna volcano (Italy), paper presented at IAVCEI General Assembly, Int. Assoc. of Volcanol. and Chem. of the Earth's Inter., Puerto Vallarta, Mexico, Jan. 19-24, 1997.
- Phelan, J., D.L. Finnegan, D.S. Ballantine, and W.H. Zoller, Airborne aerosol measurement in the quiescent plume of Mount St. Helens: September, 1980, *Geophys. Res. Lett.*, **9**, 1093-1096, 1982.
- Quisefit, J.P., G. Bergametti, D. Tedesco, J. Pinart, and J.L. Colin, Origin of particulate potassium in Mt. Etna emission before and during the 1983 eruption, *J. Volcanol. Geotherm. Res.*, **35**, 111-119, 1988.
- Shinohara, H., J. Toshimichi, and S. Matsuo, Partition of chlorine compounds between silicate melt and hydrothermal solutions, I, Partition of NaCl-KCl, *Geochim. Cosmochim. Acta*, **53**, 2617-2630, 1989.
- Sigvaldason, G., and N. Oskarsson, Chlorine in basalts from Iceland, *Geochim. Cosmochim. Acta*, **40**, 777-789, 1976.
- Stoiber, R.E., and W.I. Rose Jr, The geochemistry of Central American volcanic gas condensates, *Geol. Soc. Am. Bull.*, **81**, 2891-2911, 1970.
- Symond, R.B., W.I. Rose, G.J.S. Bluth, and T.M. Gerlach, Volcanic-gas studies: Methods, result, and applications, in *Volatiles in Magmas*, Rev. Mineral., vol. 30, edited by M.R. Carroll and J.R. Holloway, pp. 1-66, Mineral. Soc. of Am., Washington, D.C., 1994.
- Tanguy, J.C., and G. Kieffer, Les éruptions de l'Etna et leur mécanismes, *Mem. Soc. Geol. Fr.*, **163**, 239-252, 1993.
- Tanguy, J.C., M. Condomines, and G. Kieffer, Evolution of the Mount Etna magma: Constraints on the present feeding system and eruptive mechanism, *J. Volcanol. Geotherm. Res.*, **75**, 221-250, 1997.
- Thordarson, T., and S. Self, Sulfur, chlorine and fluorine degassing and atmospheric loading by the Roza eruption, Columbia River Basalt Group, Washington, USA, *J. Volcanol. Geotherm. Res.*, **74**, 49-73, 1996.
- Varekamp, J.C., E. Thomas, M. Germani, and P. Busek, Particle geochemistry of volcanic plumes of Etna and Mount St. Helens, *J. Geophys. Res.*, **91**, 12333-12248, 1986.

---

M.F. Le Cloarec, Centre des Faibles Radioactivités, CNRS/CEA, Avenue de la Terrasse, 91198 Gif sur Yvette Cedex, France. (e-mail: Marie-Francoise.Le-Cloarec@cfr.cnrs.gif.fr)

M. Pennisi, Istituto di Geocronologia e Geochimica Isotopica, CNR, via Cardinale Maffei 36, 56127 Pisa, Italy. (e-mail: iggi@iggi.pi.cnr.it)

(Received October 10, 1997; accepted October 16, 1997.)