The 5 April 2003 paroxysm at Stromboli: a review of geochemical observations

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Abstract

This paper reviews the published geochemical variations observed during the 2002–2003 eruption at Stromboli volcano. At the end of 2002, a new eruption began at Stromboli with a lava flow that lasted until the end of July 2003. On 5 April 2003 an explosive paroxysm occurred with the ejection of bombs that reached the village of Ginostra, about 4 km from the craters. During the eruption, specific variations in chemical composition of ground waters and summit fumaroles were recorded before the explosion, most of them for the first time. The water pH decreased significantly (0.5 units) and the dissolved CO_2 increased in two thermal wells (Cusolito and Zurro) located near Stromboli harbor from March until 5 April. Peaks in the dissolved He were also observed at all the sampling sites. All of these changes in the thermal aquifer suggested a pressurization of the system due to the degassing of a volatile-rich magma at depth. In the summit area the SO_2/HCl and SO_2/HF ratios in the plume increased suddenly between 1 and 3 April due to the degassing of an S-rich magma that was approaching the shallow levels of the plumbing system, and this was involved in the explosion that occurred a few days later. This eruption was the first at Stromboli to be analyzed using geochemical models. The variations observed in the basal aquifer and in the summit area occurred on very different timescales: a few weeks and few days, respectively.

Introduction

The Italian volcano Stromboli is internationally famous due to its persistent activity characterized by mild explosions every 15–20 minutes fed by three vents located in the crater area, at an elevation of 700 m a.s.l. The present-day activity is sustained by a degassed, crystal-rich shoshonitic magma residing in the shallow plumbing system of the volcano (Landi et al., 2006). This magma is continuously crossed by gas bubbles coming from a crystal-poor, volatile-rich magma located in the deep portion of the feeding system, whose ascent and bursting is probably responsible for the strombolian activity at the surface (Ripepe et al., 2002; Chouet et al., 2003; Metrich et al., 2005). Sometimes this persistent activity is interrupted by lava effusion onto the Sciara del Fuoco (SDF)

flank and/or by more violent and dangerous paroxysmal explosions. The latter result in the ejection of bombs that often reach a few kilometers from the crater area and comprise golden pumice and mingled blocks due to the coexistence of dark-colored, crystal-rich scoria, and crystal-poor pumice (Landi et al., 2006).

The persistent volcanic activity at Stromboli provides a unique opportunity for scientists to develop and test new models as well as to apply the established ones. Work performed during the past 10 years has revealed the great potential of fluid geochemistry to both explain and predict the degassing mechanisms and eruptive activity of this volcano. Geochemical monitoring in Italian volcanic areas has demonstrated the usefulness of investigating plume chemistry (Aiuppa et al., 2002; 2004; Allard et al., 2004), He and C isotopes in both gases and waters (Caracausi et al., 2003; Capasso et al., 2005; Rizzo et al., 2006; Federico et al., this volume), and soil gas emissions (Badalamenti et al., 2004; Carapezza et al., 2004). Similar investigations carried out in other active volcanoes such as Masaya (and others in this list) in Nicaragua (Duffell et al., 2003), Galeras in Colombia (Sano et al., 1997), Sakurajima in Japan (Hirabayashi et al., 1986), and Oshima Island in Japan (Sano et al., 1988) have demonstrated that geochemical studies can be used to predict the eruptive activity of a volcano. For example, a marked increase in the SO_2/HCl ratio in the plume was recorded prior to the 23 April 2001 explosion at Masaya, and this was attributed to scrubbing of water-soluble magmatic gases by a rejuvenated hydrothermal system (Duffell et al., 2003). Helium-isotope variations were recorded in high-temperature fumaroles during an increase in the activities of the Oshima Island and Galeras volcanoes, and were considered indicative of the injection of mantle-derived volatiles (Sano et al., 1988; Sano et al., 1997). A marked increase in helium concentration in fumarolic samples at Galeras was also recorded during the same investigative period preceding its eruptive activity (Fischer et al. 1997). The H_2 concentration measured in gas from a hot spring at Sakurajima increased a few weeks before the resumption of intense explosive activity (Hirabayashi et al., 1986). These reports represent a very small proportion of the many examples of geochemical variations observed in volcanic systems worldwide that testify to the usefulness of geochemical investigations in the volcanic natural environment.

At Stromboli, a preliminary geochemical investigation carried out at the end of 1992 by Capasso and Carapezza (1994) identified two areas characterized by anomalous CO_2 soil emissions: (1) Pizzillo, located in the northeastern part of the island near the inhabited area, and (2) Pizzo Sopra La Fossa (PSF), along the crater rim. These anomalies were investigated by Carapezza and Federico (2000), whose systematic CO_2 soil flux survey aimed at identifying the main volcanotectonic structures controlling the gas ascent from depth. Automatic stations for continuously monitoring of CO_2 soil flux and environmental parameters (STR01 and STR02) were installed in July 1999 at the

two anomalous sites of Pizzillo and PSF (Carapezza and Inguaggiato, 2001). The volcanotectonic structure has been further investigated by Finizola et al. (2002, 2003), who identified a summit hydrothermal system beneath the La Fossa crater depression using self-potential, temperature, CO_2, and fumarolic-fluids measurements. The investigation of gases dissolved in water revealed a contribution of magmatic fluids in some thermal wells located near the inhabited area of Stromboli that showed an unexpected high $^3He/^4He$ ratio (≈4.1 Ra; Inguaggiato and Rizzo, 2004), suggesting the presence of a basal hydrothermal system that needed to be monitored. Indeed, previous investigations had established that the helium-isotope signature for Stromboli was typically 3.0–3.5 (Carapezza et al., 2000).

The monitoring of gases for 6 years at site SC5 in the summit area (a fumarole located in the anomalous area of PSF) showed a clear magmatic contribution to the emitted fluids (Carapezza and Federico, 2000). The total plume output of acid gases and SO_2 was quantified several times by airborne and ground-based filter-pack sampling combined with correlation spectrometry measurements (Allard et al., 1994, 2000; Aiuppa et al., 2005), which revealed the great importance of evaluating the budget of gases released to the atmosphere and of estimating the magma volume that participated in a recharge toward the surface.

In this paper we present a review of the geochemical variations observed during the 2002–2003 eruptive period at Stromboli, focusing on the paroxysm that occurred on 5 April 2003.

Eruptive activity during 2002–2003

The 2002–2003 volcanic activity of Stromboli was characterized by a new flank eruption that started on 28 December 2002 and lasted until 22 July 2003. Since May 2002, a considerable increase in strombolian activity coupled with small lava overflows from the summit craters was recorded by an INGV-CT web camera located at PSF (Bonaccorso et al., 2003). Apart from the spectacular but innocuous lava flow that started on 28 December from a fissure located in SDF between 550 and 650 m a.s.l., this eruption will be remembered for two dangerous phenomena that caused concern to scientists and the Italian Civil Defence: (1) flank landslides of SDF and the associated tsunami that caused damage around the island on 30 December 2002 (Bonaccorso et al., 2003; Pino et al., 2004); and (2) the explosive paroxysm that occurred at the craters on 5 April 2003, which lasted a few minutes and was characterized by a vertical gas emission into the atmosphere accompanied by the fallout of bombs and blocks that reached the village of Ginostra, and was the strongest event recorded at Stromboli since the 1930 paroxysm (Rittmann, 1931; Barberi et al., 1993). Similarly to previous energetic events that occurred in the known history of the volcano, the explosion was accompanied by the presence of two HK-basaltic components that

resulted from the sudden ascent of crystal-poor, gas-rich magma through the resident magma, which is degassed and crystal-rich (Metrich et al., 2001; Landi et al., 2004; Metrich et al., 2005; Rosi et al., 2006). It is worth noting that the paroxysm occurred while the lava emission was still in progress from a vent located at 600 m a.s.l., and that the summit craters were clogged with debris (Rosi et al., 2006).

After 5 April, normal strombolian activity gradually resumed at the summit craters due to the progressive ascent of the magma level in the conduits. This resulted in effusive vents gradually moving up the slope until the flow field was active in SDF (Calvari et al., 2006).

Methods

Thermal waters have been collected since 1999 from three wells (named Cusolito, Fulco, and Zurro) with depths from a few to a few tens of meters (Fig. 1) located in the northeastern part of Stromboli about 5 km from the craters. The sampling frequency was once per month during the normal strombolian activity, and increased up to twice per week during the 2002–2003 eruption. All of the collected waters have been analyzed in the INGV-PA laboratories for their chemical composition, as have the He and C isotopic compositions of the dissolved gases. The sampling and analytical techniques are described by Capasso and Inguaggiato (1998), Inguaggiato and Rizzo (2004), and Capasso et al. (2005a). The chemical content of dissolved gases is expressed as cubic centimeters of gas per liter of water at standard temperature and pressure conditions ($cc \cdot l^{-1}$ STP). Helium isotopes are reported as Rc/Ra, which is the ratio corrected for air contamination on the basis of $^{4}He/^{20}Ne$ ratio measured in the same gas (Inguaggiato and Rizzo, 2004). Carbon isotopic composition is reported as $\delta^{13}C$ in parts per thousand vs PDB (Capasso et al., 2005b). Temperature, pH, conductivity, and Eh have been directly measured in the field during water sampling.

The carbon dioxide flux and certain meteorological parameters (e.g. soil temperature and humidity) have been measured hourly by an automatic station (STR02; Fig. 1) installed in 1999 at PSF. Further details about the technical specifications of the system are provided in Carapezza et al. (2002, 2004), Brusca et al. (2004), Federico et al. (this volume), and Madonia et al. (this volume).

The contents of SO_2, HCl, and HF (expressed in micrograms per cubic meter) in the Stromboli plume were measured using diffusive (passive) samplers equipped with an NaOH-impregnated sorbent. These diffusive tubes were exposed to the atmosphere (protected from rainwater) at PSF (Fig. 1) at 1.0–2.5 meters above ground for a duration determined by the ability to climb in the crater area. After exposure, filters were eluted in H_2O-H_2O_2 solution, then analyzed for Cl^{-}, F^{-}, and SO_4^{2-} by ion chromatography. This technique for volcanic plume monitoring is described by Aiuppa and Federico (2004) and Aiuppa et al. (2004).

Geochemical changes heralding the 5 April paroxysm

Most of the gases released from the magma in a volcanic system are degassed to the atmosphere via the plume that is continuously emitted from the craters. However, some of this gas is also released near the crater area via fractures connecting the volcanic conduit with the surface or diffusively from the soil and at the base of the volcanic cone, and near the coast where gas of deeper provenance interacts with the shallow aquifer to generate thermal waters. The shallow geothermal strombolian aquifer has been intercepted by a few wells drilled in the northeastern part of the island near the harbor of Stromboli (Grassa et al., this volume).

This study focused on the gases discharged from the soil in the crater area and from the plume emitted from the craters. We also investigated the thermal waters in order to better understand gas–water interaction processes and their possible relation with the volcanic activity.

Basal thermal aquifer

The collected thermal waters have a temperature ranging from 34.7 °C (Zurro well) to 44 °C (Cusolito well) and contain between 9000 and 40,000 mg·l^{-1} dissolved salts due to the variable contribution of seawater to the aquifer. The wells have a depth ranging from a few to a few tens of meters, depending on the altitude at which they are drilled, because the water table is constantly a few meters below sea level. Interactions between the rocks and deep hot waters have been confirmed by the anomalous enrichment in some elements with respect to a mixing between shallow meteoric waters and seawater (see Capasso et al., 2005a; Grassa et al., this volume). The pH of collected waters varies with the investigated site, but is always less than the typical value of marine water (pH=8.3). During the 2002–2003 eruption, the pH ranges were 6.27–6.86, 6.17–6.56, and 6.7–7.3 at the Cusolito, Fulco, and Zurro wells, respectively. These values are consistent with dissolution in the water of acid species such as carbon dioxide. Indeed, the CO_2 in dissolved gases varied with the sampled well, being 44–81, 76–210, and 6–91 cc·l^{-1} STP at Cusolito, Fulco, and Zurro, respectively. These values are well above the normal content of CO_2 dissolved in air-saturated seawater (≈0.25 cc·l^{-1} STP). These anomalous values of dissolved CO_2, coupled with the $\delta^{13}C$ of CO_2 being from −9‰ to −1.1‰ vs PDB, suggest a magmatic origin of the fluids interacting with the shallow aquifer. The measured carbon-isotope values in the dissolved gases are indeed comparable with those in the crater fumaroles (Finizola and Sortino, 2003; Capasso et al., 2005; Federico et al., this volume). The measured ranges of He content in dissolved gases were 1.99×10^{-4}–8.56×10^{-3} cc·l^{-1} STP at Cusolito, 2.05×10^{-4}–1.58×10^{-2} cc·l^{-1} STP at Fulco, and 1.86×10^{-4}–6.47×10^{-3} cc·l^{-1} STP at Zurro. The carbon dioxide content was sensibly higher than that in air-

saturated water (ASW; 4.55×10^{-5} cc·l^{-1} STP). Helium-isotope values were in the range 3.49–4.56 Rc/Ra, confirming the magmatic signature of the dissolved gases in the thermal waters. Specifically, the recorded values were higher than those measured at the SC5 crater fumarole (≈ 3 Ra; Carapezza and Federico, 2000; Inguaggiato and Rizzo, 2004; Federico et al., this volume) and comparable to those at the active fumarole field located near the northeastern crater (4.3 Ra; Finizola and Sortino, 2003). Finally, the O_2 content dissolved in collected waters never exceeded 2.8 cc·l^{-1} STP, while ^{4}He/^{20}Ne was in the range 1–10.66 (in ASW: O_2=6.37 cc·l^{-1} STP, ^{4}He/^{20}Ne=0.285), suggesting a low atmospheric contribution. Therefore, an interaction process between deep magmatic gases and shallow waters is well recognized, confirming the usefulness of monitoring these basal thermal wells to provide evidence of anomalous degassing related to depressurization upon ascent of new magma batches, such as the ones that trigger explosive paroxysms.

These geochemical parameters have been regularly monitored since 1999, and have displayed anomalous variations during periods of intense strombolian activity and before the onset of the 2002–2003 eruption (Carapezza et al., 2004a; Capasso et al. 2005; Federico et al., this volume). We now report the most indicative variations recorded across the 5 April paroxysm.

Starting from the end of February 2003, the pH progressively decreased and the dissolved CO_2 simultaneously increased in Cusolito and Zurro waters (Fig. 2). These variations were also accompanied in all the monitored wells by the amount of He dissolved in water peaking at one to two orders of magnitude higher than the average (Fig. 3). Also, the Fulco water showed synchronous anomalies in pH, temperature, and dissolved CO_2. An experimental continuous station, designed by the IGG-CNR, Pisa, was installed in this well at the beginning of February. The temperature, pH, conductivity, Eh, and dissolved CO_2 and CH_4 were measured every second (for technical details, see Carapezza et al., 2004b). In the period preceding the 5 April paroxysm, temperature, and dissolved CO_2 increased, and pH decreased. These trends reversed soon after the explosion, in agreement with data from the intermittent sampling.

An anomalous ^{4}He/^{20}Ne peak of more than 10 was also observed at Cusolito about 2 weeks before the 5 April paroxysm (Fig. 4), which had never been measured before in the basal thermal aquifer. This suggests a decrease in the shallow atmospheric component of the incoming CO_2 also dissolved in the water. The observed variations suggested a pressurization of the shallow geothermal system by the degassing of magmatic gases at depth. Following the explosive event, He and CO_2 contents as well as ^{4}He/^{20}Ne ratios decreased toward the average values recorded before the paroxysm, while the water pH returned to 6.6 and 6.9 at the Cusolito and Zurro wells, respectively (Figs. 2, 3, and 4). Helium isotopes displayed almost synchronous variations at all the sampling sites, suggesting that

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they had a common deep magmatic source. At the end of January (Fig. 5), the ^{3}He/^{4}He ratio reached the highest value ever measured at Stromboli of 4.56 Ra (Capasso et al., 2005; Federico et al., this volume), after which a progressive decrease in ^{3}He content characterized the Cusolito, Fulco, and Zurro waters until the end of March, with the trend thereafter reversing at Fulco and Zurro. Particularly, on 23 March the value at the Fulco well reached its lowest value of 3.58 Ra. The Cusolito site displayed a different trend, showing a minimum ^{3}He/^{4}He ratio of 3.83 Ra on 5 April. Following the paroxysm, helium isotopes showed almost identical trends in all the thermal wells, with pulsing variations that accompanied the resumption of normal strombolian activity.

The variations observed in ^{3}He/^{4}He ratios can be ascribed either to a variable contribution of a crustal ^{4}He-rich term mixed with the magmatic component or, more likely, to a variable extent of magma degassing at depth, in which the decrease in helium-isotope ratios could be due to the loss of ^{3}He during magma degassing and depressurization. In contrast, increases in ^{3}He/^{4}He ratios can be ascribed to a replenishment of a new deep magma batch that is rich in ^{3}He.

Similar variations in helium-isotope ratios were also recorded at the Oshima Island and Galeras volcanoes during an increase in the volcanic activity, and were unequivocally interpreted as indicative of the injection of mantle-derived volatiles (Sano et al., 1988; Sano et al., 1997). In view of the observed variations, the ^{3}He/^{4}He ratio peak recorded at the end of January would suggest the degassing of a new deep magma batch that is rich in ^{3}He, which probably rose toward the surface and fed the lava effusion. It cannot be excluded that this new magma batch was involved in the paroxysm that occurred 2 months later. This is supported by the lack of further increases in helium-isotope ratios before then. The ^{3}He/^{4}He ratio decrease observed in March at the Fulco well could be due to a minor interaction of magmatic gases with the shallow aquifer.

Summit area

Continuous monitoring at an automatic station since July 1999 revealed that the daily average CO_2 soil flux at PSF was 5000–6000 g·m^{-2}·d^{-1} during periods of normal strombolian activity. There was an anomalous increase in CO_2 released from soil for 1 week before the onset of the 2002–2003 eruption, which reached values in excess of 80,000 g·m^{-2}·d^{-1} (Carapezza et al., 2004; Federico et al., this volume), the highest ever measured since its installation. It is noteworthy that there was no lava effusion at Stromboli from 2000 to 2002. After the onset of the 2002–2003 eruption, the CO_2 flux decreased to an average value of 10,000 g·m^{-2}·d^{-1} without further variations as clear as those recorded before 28 December 2002. High values were recorded again in January 2003, but they were only nearly half those recorded before the eruption onset (Fig. 6). A slight increasing trend was observed for about 1 month before 5 April (Fig. 6), reaching about 20,000 g·m^{-2}·d^{-1}. After the

paroxysm the CO_2 flux decreased slowly to 7000 $g \cdot m^{-2} \cdot d^{-1}$ and remained nearly constant throughout the remaining eruptive period.

In the summit area of Stromboli, the clearest signals heralding the 5 April paroxysm were in the plume chemistry. Previous investigations of its chemical composition demonstrated that SO_2 was the third major component (after H_2O and CO_2) of the volatile phase degassed from magma (Allard et al., 1994). Minor species degassed from magma at shallow depth are acid gases such as HCl and HF, with the latter coupled with SO_2 collected in the crater rim area (Fig. 1) using diffusive tubes (see analytical techniques section) since April 1. During the investigated period, the SO_2 content in the atmosphere surrounding the craters ranged between 6500 $\mu g \cdot m^{-3}$ before the paroxysm and 42 $\mu g \cdot m^{-3}$ at the end of September, when the strombolian activity had already resumed and the eruption had ended about 2 months previously. These values exceed the atmospheric background at Stromboli (17 $\mu g \cdot m^{-3}$), suggesting a magmatic origin of SO_2 as the unique explanation of these measured high contents. In contrast, HCl and HF appeared to vary randomly during the observation period, with concentrations ranging from 77 to 1175 $\mu g \cdot m^{-3}$ and from 20 to 207 $\mu g \cdot m^{-3}$, respectively. An analysis by Aiuppa and Federico (2004) indicated that the recorded data were unlikely to be influenced by wind, rainfall, or barometric pressure.

Figure 7 shows temporal variations in the SO_2/HCl and SO_2/HF molar ratios during the investigated period. Both ratios increased rapidly a few days before the 5 April explosion, with SO_2/HCl increasing from 4.5 to about 9 in less than 1 day. The values of SO_2/HCl before the paroxysm were the highest ever measured in the area since the development of this technique, and significantly above the normal passive degassing at Stromboli (Allard et al., 1994; 2000; Burton et al., 2001; Burton and Murè, 2002), suggesting an involvement of degassing of an SO_2-rich magma just prior to the explosion. This hypothesis is strongly supported by the observations of Bertagnini et al. (2003), who ascribed the major explosion and paroxysm to the rapid ascent of primitive gas-rich magma toward the shallow plumbing system (Francalanci et al., this volume). Indeed, following 5 April, SO_2/HCl and (to a lesser extent) SO_2/HF decreased to much lower values until the end of the effusion. Further decreases were observed when the strombolian activity gradually replaced the lava effusion, with the values eventually stabilizing at around the average values characteristic of normal passive degassing at Stromboli.

Concluding remarks

The Stromboli 5 April explosive paroxysm was preceded by geochemical changes in both the basal thermal aquifer and the crater area. The main anomalies were recorded from 1 month to a few days before the explosion. From the beginning of March, the pH of the thermal waters of Cusolito and

Zurro wells progressively decreased, with a corresponding increase in dissolved CO_2. A significant peak in dissolved He was also observed in all the wells by middle March, followed by a marked decrease in the $^3He/^4He$ ratio at the Fulco and Zurro sites. The CO_2 released from soil measured at PSF (in the summit area) increased moderately from 1 month before the paroxysm. A few days before 5 April, the SO_2/HCl and SO_2/HF ratios in the plume suddenly increased, which had never been recorded previously. After the major explosion, all the monitored geochemical parameters returned to their average values contemporarily to the resumption of normal strombolian activity and the end of the eruption.

These geochemical variations observed across the 5 April event identified – 1 month in advance – the progressive pressurization of the basal thermal aquifer due to the degassing of a volatile-rich magma at depth. The plume chemistry 40–60 hours before the paroxysm indicated an important degassing event of the S-rich magma approaching the shallow plumbing system, which was probably involved in the subsequent explosive event. The resumption of normal strombolian activity was not accompanied by further input of magma.

The geochemistry at Stromboli was monitored from 1999 until late 2002, during which no lava effusion occurred. This permitted the collection of a set of data representative of a long intereruption period that has successfully been used as a reference background to recognize anomalies heralding important changes in the eruptive regime of the volcano. Despite the dense geophysical network operating at Stromboli, no geophysical precursors were observed for the 5 April paroxysm, with the only forerunning phenomena being the described geochemical variations. This confirms the crucial importance of fluid geochemistry in the monitoring of open-conduit volcanoes, and encourages further developments in this area.

Acknowledgments

References

Aiuppa, A., Federico, C., 2004. Anomalous magmatic degassing prior to the 5th April 2003 paroxysm on Stromboli. Geophysical Research Letters 31 (L14607). doi:10.1029/2004GL020458.

Aiuppa, A., C. Federico, A. Paonita, G. Pecoraino, and M. Valenza (2002),S, Cl and F degassing as an indicator of volcanic dynamics: the 2001 eruption of Mount Etna, *Geophys. Res. Lett., 29-11* S4-1/S4-4.

Aiuppa, A., C. Federico, G. Giudice, S. Gurrieri, A. Paonita, M. Valenza (2004), Plume chemistry provides insights into mechanisms of sulfur and halogen degassing in basaltic volcanoes, *Earth Planet. Sci. Lett., 222*, 469–483.

A. Aiuppa, S. Inguaggiato, A. J. S. Mcgonigle, M. O'dwyer, C. Oppenheimer, M. J. Padgett, D. Rouwet and M. Valenza (2005), H2S fluxes from Mt. Etna, Stromboli, and Vulcano (Italy) and implications for the sulphur budget at volcanoes, *Geochimica et Cosmochimica Acta*, Vol. 69, No. 7, pp. 1861–1871.

Allard, P., J. Carbonelle, N. Metrich et al. (1994), Sulphur output and magma degassing budget of Stromboli volcano, Nature, 368, 326–330.

Allard, P., A. Aiuppa, H. Loyer et al. (2000), Acid gas and metal emission rates during long-lived basalt degassing at Stromboli volcano, Geophys. Res. Lett., 27, 1207–1210.

Allard, P., Burton, M., and Muré, F., Spectroscopic evidence for a lava fountain driven by previously accumulated magmatic gases, Nature, 433, 407 410, 2004.

Badalamenti, B., N. Bruno, T. Caltabiano, F. Di Gangi, S. Giammanco, and G. Salerno (2004), Continuous soil CO_2 and discrete plume SO_2 measurements at Mt. Etna (Italy) during 1997-2000: a contribution to volcano monitoring, *Bull. Volcanol. 66*, 80-89, DOI 10.1007/s00445-003-0305-y.

Barberi, F., M. Rosi, and A. Sodi (1993), Volcanic hazard assessment at Stromboli based on review of historical data, Acta Vulcanol., 3, 173–187.

Bertagnini, A., N. Me´trich, P. Landi, and M. Rosi (2003), Stromboli volcano (Aeolian Archipelago, Italy): An open window on the deep-feeding system of a steady state basaltic volcano, J. Geophys. Res., 108(B7), 2336, doi:10.1029/2002JB002146.

Bonaccorso, A, S. Calvari, G. Garfì, L. Lodato, and D. Patanè (2003), Dynamics of the December 2002 flank failure and tsunami at Stromboli volcano inferred by volcanological and geophysical observations, *Geophys. Res. Lett., 30* (18) 1941 doi: 10.1029/2003GLO17702.

Brusca, L., S. Inguaggiato, M. Longo, P. Madonia, and R. Maugeri (2004) The 2002--2003 eruption of Stromboli (Italy): Evaluation of the volcanic activity by means of continuous monitoring of soil temperature, CO_2 flux, and meteorological parameters, *Geochemistry, Geophysics, Geosystems 5(12),* doi: 10.1029/2004GC000732. issn: 1525-2027.

Burton, M., P. Allard, L. Brusca, and F. Mure` (2001), High resolution spectroscopic analysis of volcanic gas composition during passive and explosive degassing at Stromboli volcano, Italy, paper presented at the Assembly, Eur. Geophys. Soc., Nice, France, 25 March.

Burton, M., and F. Mure` (2002), Helicopter-borne FTIR measurements of the summit crater plume of Stromboli, open file report, INGV-CT, Catania, Italy.

S. Calvari, L. Spampinato, L. Lodato (2006), The 5 April 2003 vulcanian paroxysmal explosion at Stromboli volcano (Italy) from field observations and thermal data, *J. Volcanol. Geotherm. Res.,* 149, 160– 175.

Capasso, G., and M.L. Carapezza (1994), A geochemical survey of Stromboli, *Acta Volcanol., 6,* 52–53.

Capasso, G., and S. Inguaggiato (1998), A simple method for the determination of dissolved gases in natural waters. An application to thermal waters from Vulcano Island, *Appl. Geochem. 13,* 631-642.

Capasso, G., M.L. Carapezza, C. Federico, S. Inguaggiato, and A. Rizzo (2005), Geochemical monitoring of the 2002–2003 eruption at Stromboli volcano (Italy): precursory changes in the carbon and helium isotopic composition of fumarole gases and thermal waters, *Bull. Volcanol., 68,* 118–134 DOI 10.1007/s00445-005-0427-5.

Capasso, G., R. Favara, F. Grassa, S. Inguaggiato, and M. Longo (2005b), On-line technique for preparing and measuring stable carbon isotope of total dissolved inorganic carbon in water sample ($\delta^{13}C_{TDIC}$), *Annals Geophys. 48,* 159-166.

Caracausi, A, R. Favara, S. Giammanco, F. Italiano, P.M. Nuccio, A. Paonita, G. Pecoraino, and A. Rizzo (2003), Mount Etna: Geochemical signals of magma ascent and unusually extensive plumbing system, *Geophys Res Lett 30 (2),* 1057 doi: 10.1029/2002GL015463.

Carapezza, M L, and C. Federico (2000), The contribution of fluid geochemistry to the volcano monitoring of Stromboli, *J. Volcanol. Geotherm. Res., 95,* 227-245.

Carapezza, M.L., S. Inguaggiato (2001), Interaction between thermal waters and CO2-rich fluids at Stromboli volcano (Italy), Proc. WRI-10, Rotterdam, Balkema, 2, 791-794.

Carapezza, M. L., M. Guidi, and S. Inguaggiato (2002), Soil CO2 degassing on Stromboli island: Influence of environmental parameters and insights on volcanic activity, paper presented at EGS 27th General Assembly, Eur. Geophys. Soc., Nice, France.

Carapezza, M L, S. Inguaggiato, L. Brusca, and M. Longo (2004a), Geochemical precursors of Stromboli 2002-2003 eruptive events *Geophys Res Lett 31 (7),* 10.1029/2004GL019614.

Carapezza, M.L., R. Cioni, M. Guidi, L. Pruiti, and A. Scozzari (2004b), Experimentation of an automatic continuous monitoring station in a thermal well of Stromboli volcanic island (Italy). Proc.

WRI-11, 1, R. B. Wanty and R. R. Seal eds., Rotterdam, Balkema, 95-99.

Chouet, B., P. Dawson, T. Ohminato, M. Martini, G. Saccorotti, F. Giudicepietro, G. De Luca, G. Milana, and R. Scarpa (2003), Source mechanisms of explosions at Stromboli determined from moment tensor inversions of very-long-period data, J. Geophys. Res., 108 (B1), 2019, doi:10.1029/2002JB001919.

Duffell, H. J., Oppenheimer C., Pyle, D. M., Galle, B., McGonigle A., Burton M. R. (2003), Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua, *J Volcanol Geotherm Res* 126, 327-339.

Finizola A, Sortino F, J-F. Lénat, Valenza M (2002), Fluid circulation at Stromboli volcano (Aeolian Island, Italy), from self-potential and CO2 surveys. *J Volcanol Geotherm Res* 116(1–2):1–18.

Finizola, A., F. Sortino, J-F. Lénat, M. Aubert, M. Ripepe, and M. Valenza (2003), The summit hydrothermal system of Stromboli: New insights from self-potential, temperature, CO2 and fumarolic fluids measurements, with structural and monitoring implications, Bull. Volcanol., 65, 486-504, doi:10.1007/s00445-003-0276-2.

Fischer, T.P.. Arehart, G.B., Counce. D.. Sturchio. N.D. and Williams. S.N.. 1997. The chemical and isotopic composition of fumarolic gases and spring discharges from Galeras Vozano. Colombia. In: J. Stix. M.L. Calvache V. and S.N. Williams (Editors), Galeras Volcano, Colombia: Interdisclipinary Study of a Decade Volcano. *J. Volcano]. Geotherm. Res*. 77: 229-253.

Hirabayashi, J., Ossaka, J., Ozawa, T. (1986), Geochemical study on volcanic gases at Sakurajima volcano, Japan. *J. Geophys. Res*. 91, B12, 167-176.

Inguaggiato, S., and A. Rizzo (2004), Dissolved helium isotope ratios in ground-waters: a new technique based on gas-water re-equilibration and its application to a volcanic area, Appl. Geochem., 19, 665-673.

Landi, P, N. Métrich, A. Bertagnini, M. Rosi (2004), Dynamics of magma mixing and degassing recorded in plagioclase at Stromboli (Aeolian Archipelago, Italy), *Contrib. Mineral. Petrol., 147,* 213-227 DOI 10.1007/s00410-004-0555-5

Landi, P., L. Francalanci, M. Pompilio, M. Rosi, R.A. Corsaro, C.M. Petrone, I. Nardini, and L. Miraglia (2006), The December 2002-July 2003 effusive event at Stromboli volcano, Italy: an insight into the shallow plumbing system by petrochemical studies, *J. Volcanol. Geotherm. Res. 155,* 263-284.

Métrich, N., A. Bertagnini, P. Landi, and M. Rosi (2001), Crystallization driven by decompression and water loss at Stromboli volcano (Aeolian Islads, Italy), *J. Petrol., 42,* 1471-1490.

Métrich, N., A. Bertagnini, P. Landi, M. Rosi and O. Belhadj (2005), Triggering mechanism at the origin of paroxysms at Stromboli (Aeolian Archipelago, Italy): The 5 April 2003 eruption, Geophys. Res. Lett., 32, L10305, doi:10.1029/2004GL022257.

Pino, N. A., M. Ripepe, and G. B. Cimini (2004), The Stromboli volcano landslides of December 2002: A seismological description, Geophys. Res. Lett., 31, L02605, doi:10.1029/2003GL018385.

M. Ripepe, A.J.L. Harris, R. Carniel, Thermal, seismic and infrasonic insights into conduit process at Stromboli volcano (2002), *J. Volcanol. Geotherm. Res.*,118, 285–297.

Rittmann, A. (1931), Der ausbruch des Stromboli am 11 September 1930, Z. Vulkanol., 14, 47–77.

Rizzo, A., A. Caracausi, R. Favara, M. Martelli, P.M. Nuccio, A. Paonita, A. Rosciglione, and M. Paternoster (2006), New insights into magma dynamics during last two eruptions of Mount Etna as inferred by geochemical monitoring from 2002 to 2005, *Geochem. Geophys. Geosyst., 7,* Q06008, DOI 10.1029/2005GC001175.

Rosi, M, A. Bertagnini, A.J.L. Harris, L. Pioli, M. Pistolesi, M. Ripepe (2006), A case history of paroxysmal explosion at Stromboli: timing and dynamics of the April 5, 2003 event, *Earth Planet. Sci. Lett. 243,* 594–606.

Sano, Y., Nakamura, Y., Notsu, K. and Wakita H. (1988), Influence of volcanic eruptions on helium isotope ratios in hydrothermal systems induced by volcanic eruptions, *Geochimica et Cosmochimica Acta*, Vol. 52, No. 5, pp. 1305–1308.

Sano, Y., Toshitaka G., Williams, S. N. (1997), Secular variations of helium and carbon isotopes at Galeras volcano, Colombia, *J. Volcanol. Geotherm. Res.*, 77, 255–265.

Figure captions

Figure 1 – Sketch map showing the locations of monitored sites (modified from http://www.celestiamotherlode.net).

Figure 2 – Temporal variations in pH and dissolved CO_2 in the waters of Cusolito (a) and Zurro (b) wells (Carapezza et al., 2004). Colored arrows indicate the decreasing trend in pH preceding the explosion. Vertical red line indicates the 5 April paroxysm.

Figure 3 – Temporal variations in dissolved He in the waters of all the sampled wells (Carapezza et al., 2004). Vertical red line indicates the 5 April paroxysm.

Figure 4 – Temporal variations in the $^4He/^{20}Ne$ ratio in the waters of the Cusolito well. Colored arrow indicates the increasing trend preceding the explosion. Vertical red line indicates the 5 April paroxysm.

Figure 5 – Temporal variations in Rc/Ra ratios in the waters of all the sampled sites (Capasso et al., 2005). Colored arrow indicates the decreasing trend preceding the explosion. Vertical red line indicates the 5 April paroxysm.

Figure 6 – Temporal variations in CO_2 flux emitted from the soil at Pizzo Sopra La Fossa, reported as 20 4-point moving averages (equating to averaging over about 1 day; Carapezza et al., 2004). Colored arrow indicates the increasing trend preceding the explosion. Vertical red line indicates the 5 April paroxysm.

Figure 7 – Temporal variations in SO_2/HCl and SO_2/HF molar ratios measured in the atmosphere surrounding the craters (Aiuppa and Federico, 2004). Horizontal bars represent time-weighted SO_2/HCl and SO_2/HF molar ratios during each exposure period, computed from the cumulative amounts of acidic gases that accumulated on the samplers throughout that time. Vertical red line indicates the 5 April paroxysm. A magnification of the first week of April is also shown to clarify the variations recorded just before the explosion.