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Continuous monitoring of hydrogen and carbon dioxide at Stromboli volcano (Aeolian Islands, Italy)

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ABSTRACT

The geochemistry of volcanic gases has been fruitfully applied to identify important changes in the volcanic activity. This study reviews the dataset of the volcanic gas survey performed during 2009 and 2010 at Stromboli (Aeolian Islands – Italy). Dry gas collection occurred discontinuously at the crater fumaroles for subsequent chemical and isotopic ($\delta^{13}C$-CO_2) analyses in the laboratory.

A tailor-made device enabled continuous survey of H_2 molar fraction and CO_2 flux on the same site. Evaluation of the raw data was performed in accordance with air temperature, atmospheric pressure, wind speed and wind direction dataset. Both MLR (Multiple Linear Regression) and FFT (Fast Fourier Transform) analyses allowed filtering the dataset from the environmental effects. The MLR analysis indicated that wind speed and air temperature affected the CO_2 flux. Changes in the atmospheric pressure promoted pumping effect of the fumarole gas and caused changes in the H_2 molar fraction. The power spectral analysis revealed daily cycles in both gases. A digital signal filtering procedure enabled minimizing the environmental effects.

This study confirmed that gas emissions from the crater fumaroles have both chemical ad isotopic composition similar to the magmatic gas phase. The results of the continuous survey showed that changes of both H_2 and CO_2 correlated with changes of the volcanic activity. Therefore, H_2 and CO_2 resulted effective tracers of the dynamics involving the plumbing system of Stromboli. Identification of changes in the gas emissions at open conduit volcanoes offers a great advance over the ground gas survey. The results of the continuous survey at Stromboli showed that H_2 could apply as an auxiliary parameter of the CO_2 flux in the surveillance programs of active volcanoes.

Key Words: *H_2 monitoring, CO_2 flux, Reducing capacity, volcano surveillance, Stromboli volcano.*

INTRODUCTION

Stromboli is the northernmost and recent volcano of the Aeolian archipelago (Italy) on the south-eastern side of the Tyrrhenian Sea (Fig. 1a). The Island of Stromboli extends in NE-SW direction along an important discontinuity, periodically injected by magma from depth (Mattia *et alii*, 2008). The base of the volcano lies 2000 m b.s.l. and the emerging part raises up to 918 m a.s.l. (i.e. Pizzo Sopra la Fossa). The volcanic cone consists of hardened lavas and eruptive scoriae that have calc-alkaline to shoshonitic composition (Francalanci *et alii*, 1989; Hornig-Kjarsgaard *et alii*, 1993; Francalanci *et alii*, 2004; Landi *et alii*, 2006).

Stromboli is a basaltic strato-volcano characterized by persistent mid explosive eruptions since 1400 – 1800 years (Rosi *et alii*, 2000). The recent eruptions of Stromboli occured in the Sciara del Fuoco from three active vent zones. The crater terrace lies at 750 m a.s.l. in a horse-shoe depression formed by several collapses of the north-western flank of the island. Strombolian explosions (VEI 1 – 2) eject scoriae and bombs for a few seconds (4 – 30 s) up to 200 m above the crater. They punctuate every 10 – 20 minutes the continuous degassing from the active vents, whereas less frequent magma overflows occur from the craters for a few hours or days. Lava effusions sporadically occur at Stromboli, moving several millions of cubic meters of magma on the Sciara del Fuoco (Landi *et alii*, 2009; Ripepe *et alii*, 2015). The most recent effusive phases took place from 28 December 2002 to 22 July 2003, from 27 February to 2 April 2007, August 2014 and July 2019.

Some major explosions interrupt the normal eruptive activity on average 0.5 – 3 times a year. Major explosions are more energetic events, and eject meter-sized ballistic blocks and lapilli far from the crater terrace. Throughout 1995 – 1999, the relevant part of the major explosions (22 out of 30 events) occurred during periods of low seismicity, lasting from weeks to a few months (Falsaperla & Spampinato, 2003). Major explosions are unpredictable and dangerous events, mainly for people climbing on the summit zone of Stromboli.

The paroxysms are the most energetic explosive events known at Stromboli (VEI 3). They are less frequent than major explosions and potentially dangerous for people and settlements in the inhabited zones of the island. Since 1874, paroxysmal events occurred at Stromboli every 4 – 5 years on average (Barberi *et alii*, 1993). The last two events took place on 3 July and 28 August 2019, respectively. The less recent paroxysmal explosions occurred on 15 March 2007 and 5 April 2003 that was the first event since 1930. Paroxysms consist of synchronous explosions from different craters forming short-living convective columns above the summit of the volcano, up to 10 km high (Aiuppa *et alii*, 2010). Paroxysmal explosions eject two magma types having contrasting textures and composition of the glass (Métrich *et alii*, 2001; Francalanci *et alii*, 2004; Bertagnini *et alii*, 2008; Landi *et alii*, 2009; Pichavant *et alii*, 2009; Métrich *et alii*, 2010). The first magma type is the degassed crystal-rich basalt (also referred to as high-porfiricity magma, or HP-magma) filling the shallow part of the plumbing system. HP-magma forms the black scoria erupted during normal explosions and lavas emitted during effusive phase of the volcano. During paroxysms, Stromboli injects crystal-poor yellowish pumices formed by gas-rich magma (i.e. LP-magma) staying in the deepest part (7 – 10 km) of the plumbing system (Rosi *et alii*, 2000; Allard *et alii*, 2000; Métrich *et alii*, 2001; Francalanci *et alii*, 2004; Bertagnini *et alii*, 2008; Allard et *alii*, 2010).

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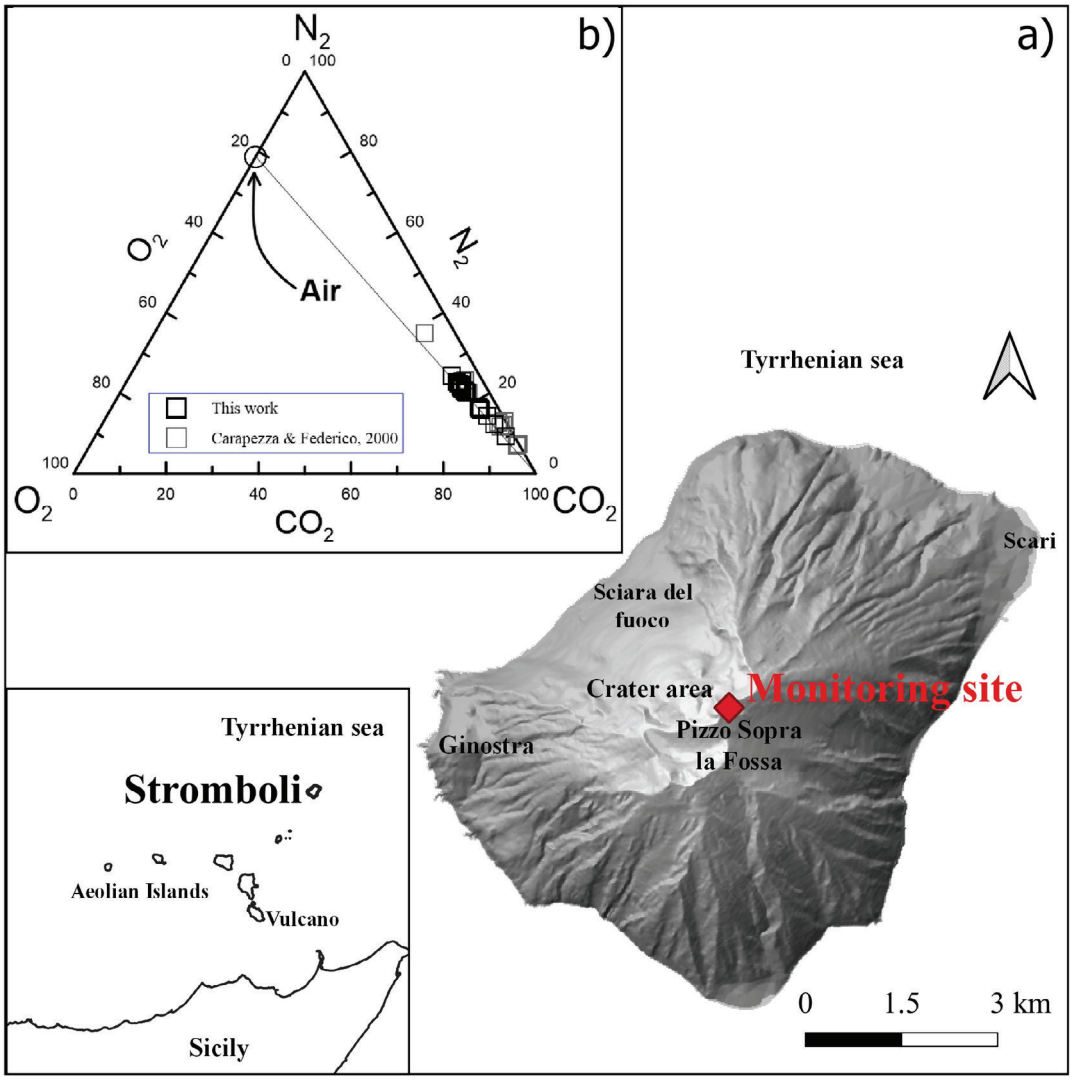

Fig. 1 - a) Map of the Island of Stromboli showing the location of the monitoring site. b) Ternary plot of the major components (N_2, O_2, and CO_2) of the gas emitted at Pizzo Sopra la Fossa site (squares) and theoretical air (circle). Chemical composition from Carapezza & Federico (2000) are shown for comparison (light grey squares).

Anomalous ground CO_2 emissions are frequent in the north-eastern part of the island and coincide with zones of high permeability along NNE-SSW volcano-tectonic discontinuities (Capasso & Carapezza, 1994; Carapezza & Federico, 2002; Finizola *et alii*, 2002; Finizola *et alii*, 2003; Cigolini *et alii*, 2005; Carapezza *et alii*, 2009; Inguaggiato *et alii*, 2013). Recent estimations showed that soil CO_2 is ~ 10% of the total CO_2 emissions at Stromboli (Carapezza & Federico, 2000; Inguaggiato *et alii*, 2013). The magmatic gases released by soils and fumaroles [e.g. carbon dioxide (CO_2), helium (He), radon (Rn), and hydrogen (H_2)] tracked the pattern of the volcanic eruptions and provided robust information for volcano surveillance (Sato & Mcgee, 1982; Baubron *et alii*, 1991; Badalamenti *et alii*, 1991; Valenza, 1993; Valenza, 1994; Barberi & Carapezza, 1994; Chiodini *et alii*, 1995; Giammanco *et alii*,1995; Diliberto *et alii*, 1996; Diliberto *et alii*, 2002; Cigolini *et alii*, 2005; Cigolini *et alii*, 2009; Granieri *et alii*, 2009; Di Martino *et alii*, 2013; Di Martino *et alii*, 2016a; Di Martino *et alii*, 2016b; Chiodini *et alii*, 2016; Morita *et alii*, 2019; Camarda *et alii*, 2019; Di Martino *et alii*, 2020; Inguaggiato *et alii*, 2020). In the past decades, the systematic recording of CO_2 flux and H_2 molar fraction tracked either the changes in the eruptive style at some basaltic volcanoes (Sato & Mcgee, 1982; Carapezza *et alii*, 2004; Carapezza *et alii*, 2009; Di Martino *et alii*, 2013) or the transition toward eruptions at some quiescent volcanoes (Badalamenti *et alii*, 1994; Barberi & Carapezza, 1994; Giammanco *et alii*, 1995).

This paper aims to correlate the results of the geochemical monitoring performed in 2009 and 2010 with the eruptive activity of Stromboli.

Moving from the pioneering investigations of Prof. Mariano Valenza on the reducing capacity of volcanic gases, this study targets H_2 and CO_2 as potential tracers of the eruptive activity of this volcano. A tailor-made automatic device allowed recording H_2 molar fraction and CO_2 flux from the crater fumaroles, provided that the selected site showed promising results for continuous geochemical monitoring of Stromboli (Carapezza & Federico, 2000; Rizzo *et alii*, 2015; Inguaggiato *et alii*, 2017b; Inguaggiato *et alii*, 2020).

METHODS

Measurements of the ground CO_2 flux are a promising tool for volcano surveillance (Gurrieri & Valenza, 1988; Barberi & Carapezza, 1994; Badalamenti *et alii*, 1994;

Boubron *et alii*, 1991; Chiodini *et alii*, 1992; Chiodini *et alii*, 1995; Chiodini *et alii*, 1998; Chiodini *et alii*, 2001; Carapezza *et alii*, 2009; Capasso et *alii*, 2017; Inguaggiato *et alii*, 2017b; Camarda *et alii*, 2019; Venturi *et alii*, 2019; Di Martino *et alii*, 2020; Inguaggiato *et alii*, 2020). The basaltic magmas achieve CO_2 saturation at the mantle depth (Kamenetski & Clocchiatti, 1996) and release huge amount of CO_2 during ascent toward the earth surface. The oxygen fugacity of magmas (f_{O_2}) changes over a wide range (10^{-16} – 10^{-8} bar) and has a pivotal role during volcanic degassing (Kelley & Cottrell, 2009). Changes in f_{O_2} affect the solubility of redox-sensitive elements, such as sulphur (S) or iron (Fe) (Carmichael & Ghiorso, 1986; Giggenbach, 1987; Scaillet *et alii*, 2005). Therefore, the reducing capacity of volcanic gases tracks the magma degassing, since f_{O_2} causes partitioning of S and Fe among melt, crystals and gases. Changes of H_2 in volcanic gases correlate with those of the redox state of magmas (Sato & Moore, 1973; Gerlach, 1991; Carapezza *et alii*, 2004; Di Martino *et alii*, 2013), because f_{H_2} depends on f_{O_2} by the water dissociation (Giggenbach, 1987). The average magmatic f_{H_2} is 10^2 – 10^{10} times higher than f_{H_2} and almost unaffected by air contamination (H_2 molar fraction in air is 0.5 ppm vol). Notable peaks in H_2 (referred to as "H_2 pulses" here) heralded the onset of volcanic eruptions (Oskarsson, 1984) and some changes in the eruptive activity of basaltic volcanoes (Carapezza & Federico, 2000; Carapezza *et alii*, 2004; Di Martino *et alii*, 2013).

A tailor-made device (Fig. 2) was installed to record the measurements of both H_2 molar fraction and CO_2 flux. The instrumentation was positioned at Pizzo Sopra la Fossa to investigate the gas released by crater fumaroles, because correlations among chemical, isotopic, and flux changes and the explosions of Stromboli were observed (Carapezza & Federico 2000; Parello *et alii*, 2000; Finizola *et alii*, 2002; Finizola *et alii*, 2003; Carapezza *et alii*, 2004; Revil *et alii*, 2004; Capasso *et alii*, 2005; Rizzo *et alii*, 2009; Rizzo *et alii*, 2015; Inguaggiato *et alii*, 2017; Inguaggiato *et alii*, 2020). The monitoring system incorporated two important techniques to collect synchronous measurements of the reducing capacity and CO_2 flux (i.e. electrochemical and optical sensors): a hydrogen fuel cell sensor (Rew Power© fuel cell - model 023) to measure H_2, and an IR spectrophotometer to measure CO_2 concentration (Edimburgh Sensors Gascard), respectively. Characterization of the fuel cell as H_2 specific sensor occurred in the laboratory through some specific tests. Technical details for the device are reported in Di Martino *et alii*, (2011) who successfully used a twin system for volcano surveillance purposes at Mount Etna (Di Martino *et alii*, 2013). The results of these tests indicated that the response time of the H_2 sensor was 90 s. The sensitivity to H_2 and the accuracy were 0.2 mV (ppm vol)$^{-1}$ and ± 5 ppm vol, respectively.

The equipment encloses an automatic pump to collect the volcanic gases for 7 minutes at a constant flux (0.5 l

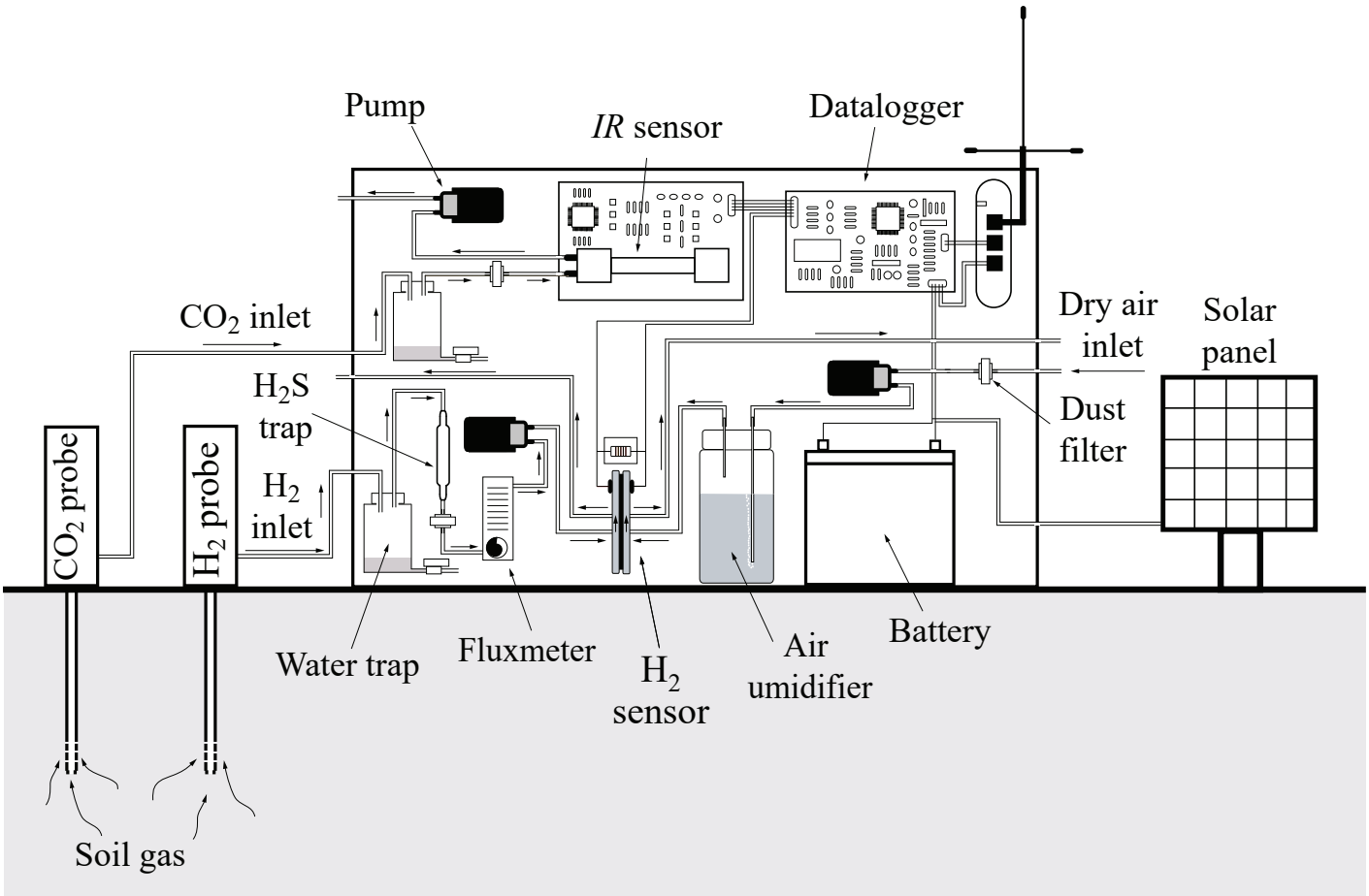

Fig. 2 - Schematic diagram of the device used for continuous survey of H_2 molar fraction and ground CO_2 flux at Stromboli. Redrawn from Di Martino et alii, 2013.

min^{-1}) through a specific probe inserted in the ground at the depth of 50 cm. The ground CO_2 flux is measured by the dynamic concentration method (Gurrieri & Valenza, 1988; Camarda *et alii*, 2006). Implementation of this method consists in measuring the CO_2 concentration in the mixture of air and ground gases formed in a cavity probe. The probe is inserted at a fixed depth in the ground (50 cm) and is open to both the air at the top and the ground gases at the bottom. By pumping the ground gases at constant rate (0.8 l min^{-1}), the system achieves the steady-state and the CO_2 concentration depends dynamically on the gas flux. An IR spectrophotometer measures the CO_2 concentration over the full range (0 – 100 vol. %). The CO_2 sensitivity was 16 mV (vol%)$^{-1}$, and the accuracy ± 2% of the full range.

Both the measurements of CO_2 flux and H_2 molar fraction were performed hourly and stored onboard in a solid memory of the data logger. The H_2-CO_2 device was deployed at Pizzo Sopra la Fossa (T ~ 90°C at 50 cm depth) since 13 May 2009. Periodic surveys throughout the 2009 – 2010 period enabled technical management of the equipment, and collection of fumarole gases (i.e. dry gases). Both chemical (He, H_2, O_2, N_2, CO, CH_4, and CO_2) and carbon isotope analyses of CO_2 (expressed in delta notation – δ^{13}C-CO_2 – using V-PDB as a reference) were performed in the laboratory by chromatographic (GC) and IRMS techniques, respectively.

RESULTS

Periodic surveys

Both chemical and carbon isotope compositions of CO_2 in the dry gases enabled characterizing the gas emission from the ground (Table 1). At the crater fumarole (Pizzo Sopra la Fossa), the CO_2 was the main gas component (range 68.6 – 80.4 vol%). The N_2 (range 15.7 – 23.9 vol %) and O_2 (range 4.0 – 6.0 vol%) followed the CO_2 molar fraction. The mass ratios of CO_2, N_2, and O_2 showed a mixing between fumarolic CO_2 and air (Fig. 1b).

The small ^{13}C-depletion of CO_2 showed the deep origin of the gases (δ^{13}C-CO_2 from -1.72‰ vs V-PDB up to -1.59‰ vs V-PDB). These values agreed with those found by previous investigations on the gas emitted by crater fumaroles (Carapezza & Federico, 2000; Carapezza *et alii*, 2004; Capasso *et alii*, 2005; Rizzo *et alii*, 2015), suggesting persistent gas releases at least since 1997 (Finizola *et alii*, 2003; Revil *et alii*, 2004; Finizola *et alii*, 2009; Carapezza & Federico, 2000). Furthermore, recent studies on melt inclusions showed δ^{13}C-CO_2 in mantle-derived magmas of Stromboli ranging from -2.8‰ to -1.5‰ vs V-PDB (Gennaro *et alii*, 2017). This study showed that δ^{13}C-CO_2 in the fumarolic agrees with the ^{13}C/^{12}C ratio from the gas released by partial melting of the mantle source beneath Stromboli. Agreement between these values and δ^{13}C-CO_2 in the fumarolic gas showed

TABLE 1

Chemical and isotope analyses of dry gases collected at Pizzo Sopra La Fossa.

Date	He (ppm vol)	H_2 (ppm vol)	O_2 (vol %)	N_2 (vol %)	CO (ppm vol)	CH_4 (ppm vol)	CO_2 (vol %)	$\delta^{13}C_{(-CO_2)}$ ‰ vs V-PDB
12.05.2009	6	377	5.47	22.14	6	2.4	71.5	-1.69
12.05.2009	10	312	5.25	21.24	4.8	1.6	73.08	--
12.05.2009	6	262	5.06	20.51	1.8	1.5	73.67	-1.66
12.05.2009	7	251	5.3	21.98	3.1	1.4	72.82	--
23.07.2009	7	77	5.46	21.43	4.3	0.8	72.77	--
23.07.2009	7	83	5.4	21.16	4.5	0.9	73.13	-1.72
23.07.2009	6	84	5.36	20.9	5	2.8	72.56	-1.66
27.08.2009	5	89	4.13	16.01	1.5	1	79.2	-1.60
27.08.2009	7	94	4.15	15.94	--	--	78.92	-1.59
27.08.2009	6	85	4.1	16	--	2.2	79.36	--
27.08.2009	5	79	4.01	15.67	0.8	2.7	79.64	--
28.10.2009	6	89	4.06	16.19	2.4	1.8	79.57	--
28.10.2009	6	92	4.06	16.26	2.4	1.6	80.43	--
28.10.2009	6	101	4.08	16.11	1.8	2.4	79.53	--
19.01.2010	4	233	4.06	16.3	1.7	2.2	80.1	--
19.01.2010	5	112	4.13	16.56	0.5	1.9	79.31	--
25.05.2010	6	99	5.76	22.45	3.4	1	70.48	--
25.05.2010	4	94	5.7	22.62	18	2.6	72.59	--
13.07.2010	6	68	5.01	20.25	51	6	74.83	--
13.07.2010	6	64	5.02	20.28	26	3.1	75.95	--
12.08.2010	4	84	5.98	23.93	11	2.6	68.62	--
12.08.2010	5	82	5.42	21.59	13	2.5	72.34	--

the negligible effects of the shallow hydrothermal system (Finizola *et alii*, 2002; Finizola *et alii*, 2003; Revil *et alii*, 2004; Finizola *et alii*, 2009) on the conceivable effects of CO_2 fractionation. Since H_2 solubility in water is 1/43 than that of CO_2 (Capasso & Inguaggiato, 1998), negligible effects of the shallow hydrothermal system can also be inferred in the H_2 molar fraction.

The He contents in the fumarole gas correlates with air (~5 ppm vol). However, the increase of He contents recorded in May 2009 (10 ppm vol) also correlated with the high H_2 in the dry gases (> 300 ppm vol). Variability of the He content agrees with literature data (Carapezza & Federico, 2000; Inguaggiato & Rizzo, 2004; Capasso *et alii*, 2005; Rizzo *et alii*, 2009; Rizzo *et alii*, 2015). These studies showed the magmatic imprint of the $^3He/^4He$ in the fumarole gas of the crater zone at Stromboli (referred to as SC5). According to these studies, the He kinetic fractionation during magma ascent caused the differences with He isotopic ratio in groundwater. However, changes in the $^3He/^4He$ ratio coincided with ^{13}C enrichment of CO_2 emitted by the crater fumarole (Rizzo *et alii*, 2015). Carapezza & Federico (2000) already showed that $^3He/^4He$ ratio in the fumarole gas of Stromboli ranged between 2.73 R_a and 3.55 R_a, with the average value 3.12 R_a during the 1992 – 1998 period ($R_a = 1.4 \cdot 10^{-6}$ is the $^3He/^4He$ ratio in the air). High content of CO_2, the notable contents of H_2 and He, and the isotopic ratios for C and He show the magmatic origin of the fumarole gas.

Continuous survey of CO_2 flux and H_2 concentration

The monitoring station performed measurements of H_2 and CO_2 at the crater fumaroles of Stromboli from 19 May 2009 to 31 October 2010. According to several authors (Finizola *et alii*, 2003; Revil *et alii*, 2004; Finizola *et alii*, 2009; Carapezza *et alii*, 2009), the N41°-oriented volcano-tectonic fracture crosses near the crater fumaroles that N64°-oriented. This zone is cracked, permeable and easily traversed by volcanic gases. Several studies found that ground degassing occurs at Stromboli mainly along these discontinuities (Finizola *et alii*, 2002; Finizola *et alii*, 2003; Revil *et alii*, 2004; Cigolini *et alii*, 2005; Cigolini *et alii*, 2007; Carapezza *et alii*, 2009; Finizola *et alii*, 2009).

Fig. 3 shows the time-series of the observed CO_2 flux, H_2 molar fraction, and environmental variables (i.e. air temperature, atmospheric pressure, wind speed, and wind direction). Downsampling of the CO_2 flux dataset occurred at 6 hours, whereas that of the H_2 molar fraction occurred at 3 hours. This difference corresponds to the inherent variability of the H_2 molar fraction. The CO_2 flux changed over two orders of magnitude throughout the surveying period (Table 2). The minimum value was 160 g m^{-2} d^{-1} while the CO_2 flux achieved the maximum in April 2010 (14252 g m^{-2} d^{-1}). The average value was 7905 g m^{-2} d^{-1} (standard deviation ± 2175 g m^{-2} d^{-1}) and CO_2 flux was persistently higher than 6000 g m^{-2} d^{-1} from July to October 2009 and often throughout 2010. The time series of CO_2 flux (Fig. 3a) showed several increasing trends between different levels of CO_2 emission (range of 4000 - 8000 g m^{-2} d^{-1}). These changes lasted a few days to some weeks, while sudden and decreasing peaks towards very low CO_2 flux values concluded in a few hours or a few days.

The instrument used at Stromboli recorded hourly the measurements of H_2 molar fraction in the fumarolic gas (Fig. 3b). The H_2 changed similarly to CO_2 flux over two orders of magnitude (Table 2). The highest H_2 molar fraction (428 ppm vol) distinguished for one order of magnitude from the average value estimated throughout the time window 2009 – 2010 (59 ppm vol ± 46 ppm vol).

Fig. 3 provides a comparison of the ways that changes of H_2 molar fraction and CO_2 flux affected the gas of the crater fumaroles. The H_2 often showed differences with the CO_2 flux and the signals looked as inherently uncorrelated. In contrast to the trends of the CO_2 flux, the H_2 time-series showed strong changes that referred to as H_2 pulses. These pulses characterized for duration of a few hours and changed the H_2 molar fraction from a few tens to several hundreds of ppm. The comparison shows that pulses with high H_2 molar fraction (up to 428 ppm vol) occurred throughout the surveying period. However, the average value estimated during 2009 (76 ppm vol) was higher than H_2 in 2010 (45 ppm vol).

DATASET ANALYSIS AND SIGNAL PROCESSING

In contrast to diffuse soil CO_2 emissions, the advection prevails over diffusion during gas flux from fumaroles (Camarda *et alii*, 2020 and reference therein). Strong pressure gradients (a few mbar in magnitude) cause gas transport in contrast to the weaker concentration gradients that activate diffusive flow. However, some atmospheric changes alter the gas flux, leading to artifacts in the time-series that mask volcano-related changes.

Identification and filtering of the environmental effects from the dataset occurred by two statistical methods. First, we applied a multiple linear regression (MLR) to identify, model, and remove the changes of both H_2 and CO_2 dependent on the environmental variables. Second, the Fast Fourier Transform (FFT) analysis allowed to identify that cyclic variations of H_2 and CO_2 not correlated with volcanic degassing. Finally, the filtered dataset classification and identification of different levels of degassing occurred by the statistical graphical approach of the probability plot (Sinclair, 1974).

The correlation among CO_2 flux, H_2 molar fraction, and some environmental variables (air temperature, atmospheric pressure, wind speed, and wind direction) has been established to better evaluate the dynamic response of the measurement site to atmospheric changes during the eruptive activity (Table 3). Environmental data were retrieved from Inguaggiato *et alii* (2017) that found

TABLE 2

Statistics of monitored parameters (this study) and environmental variables (retrieved from Inguaggiato et alii, 2017; 2020 and reference therein)

Parameter	Minimum	Maximum	Average	St. Dev
CO_2flux (g m^{-2} d^{-1})	160	14252	7905	2175
H_2 (ppm vol)	1	428	59	46
Air Temp (°C)	10	46	23	6
Atm Pressure (mbar)	893	921	913	4
Wind Speed (m s^{-1})	0	29	3	4

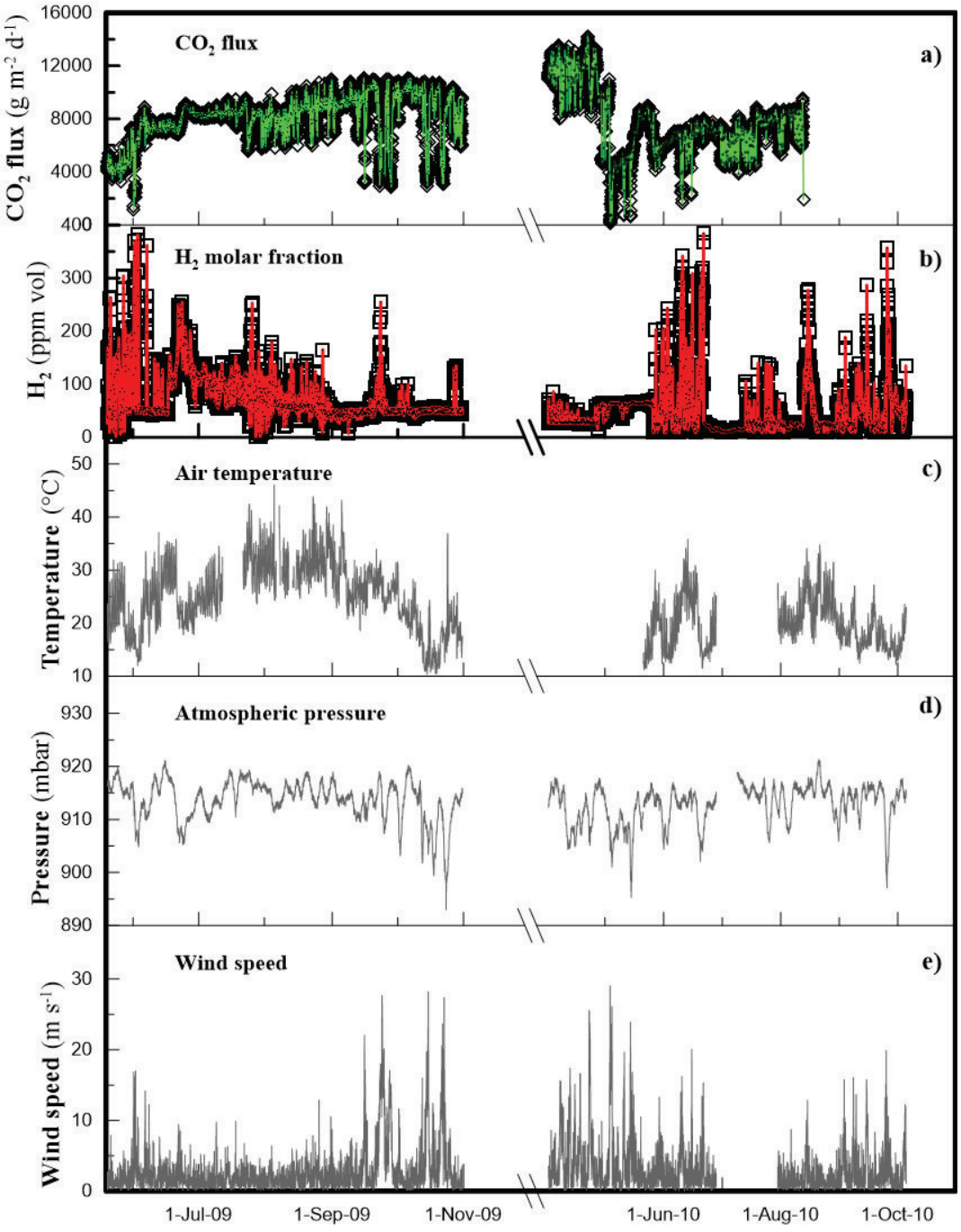

Fig. 3 - a) Time-series of the CO_2 flux measurements. Down sampled data (6 hours) are shown (green line). b) Time-series of the down sampled H_2 molar fraction (3 hours). Down sampled data (3 hours) are shown (red line). c) Time-series of the air temperature. d) Time-series of atmospheric pressure. e) Time-series of the wind speed. Dataset of atmospheric parameter were retrieved from Inguaggiato *et alii* (2020, and reference therein).

a correlation between the CO_2 flux recorded in the crater zone and the explosivity of Stromboli. A measurement subset recorded by these different stations coincided temporally and used to perform: i) the MLR on both H_2 and CO_2 raw signals, and ii) the comparison between FFT and MLR results.

The correlation provides some preliminary information on the environmental effects on the fumarole gas emissions. The values of correlation coefficients showed that changes in both air temperature and wind speed affected the CO_2 flux. The correlation (0.181) showed that CO_2 flux increased during summer, while CO_2 emissions from the crater fumarole decreased during winter due to temperature drops. A positive correlation between air temperature and soil CO_2 fluxes is a behaviour commonly noted in other active geothermal and volcanic zones (Granieri *et alii*, 2003; Camarda *et alii*, 2012). The negative correlation coefficient showed that CO_2 emissions decreased during periods of high wind speed. Wind achieved very high speed (up to 29 m s^{-1}) sporadically, whereas the average value was 3 m s^{-1}. The correlation with CO_2 flux appeared different with respect to that recognized by Laiolo *et alii* (2016) who studied the environmental effects on both radon (Rn) and CO_2 emissions at Stromboli. Temperature increases cause ground gas expansion, thus reducing the air supply that enters the sampling probe. On the contrary, the increase in wind speed favours the increase of the air that enters the probe. Therefore, the dynamic concentration of

TABLE 3

Correlation between observed H_2 molar fraction and CO_2 flux with air temperature, atmospheric pressure, wind speed, and wind direction. Dataset of the environmental variables were retrieved from Inguaggiato *et alii*, (2017, 2020 and reference therein).

	H_2 raw	**CO_2flux raw**	**Air Temp**	**Atm Pressure**	**Wind direction**	**Wind speed**
H_2 raw	1					
CO_2flux raw	-0.168	1				
Air Temp	-0.017	0.181	1			
Atm Pressure	-0.121	0.041	0.412	1		
Wind direction	0.072	-0.020	-0.113	-0.124	1	
Wind speed	0.076	-0.218	-0.100	-0.292	0.083	1

CO_2 increases and decreases, accordingly. This effect is independent form direction of the blowing wind. Actually, the CO_2 flux weakly correlated with wind direction (R = -0.02). Thus, the changes in wind speed and temperature caused different effects on different zones of Stromboli. The comparison showed that differences in the correlation between the CO_2 flux and the environmental variables can result from differences in the measurement methods. Alternative explanations involve local effects that strongly constrained the gas emissions from the ground. This paper indeed reports on the CO_2 flux measurements performed at crater fumarole, that is different from Nel Cannestra site (Laiolo *et alii*, 2016). Although local responses can affect the gas flux from the ground (Camarda *et alii*, 2016; Camarda *et alii*, 2017), the alternative assumption cannot be ruled out, i.e. differences in the measurement methods caused some differences in the correlation with the environmental changes.

The correlation analysis showed that atmospheric pressure was the environmental variable that affected the H_2 concentration in the fumarole gas (R = -0.121). The negative dependency of the correlation coefficient showed that decreases in atmospheric pressure caused the increase of H_2 concentration. This was the expected result because of changes in atmospheric pressure resulted in different pressure gradient between the ground and atmosphere. Therefore, the decrease in the atmospheric pressure promoted gas pumping from the ground (Camarda *et alii*, 2020, and reference therein).

Multiple linear regression statistic test (MLR)

The multiple linear regression analysis applied to subset consisting of the environmental dataset (Inguaggiato *et alii*, 2017; Inguaggiato *et alii*, 2019; Inguaggiato *et alii*, 2020) and both the CO_2 flux and H_2 molar fraction. Unfortunately, environmental dataset partially corresponds with the observed H_2 and CO_2 signals. However, the results of MLR analysis resulted in a useful test for the goodness of the filtering procedure.

The MLR models the contributions of several independent variables on the H_2 and CO_2 signals. The analysis predicted the values of the dependent variable (i.e. H_2 and CO_2) given a set of independent variables (i.e. air temperature, atmospheric pressure, wind speed, and wind direction). According to several authors (Granieri *et alii*, 2003; Hernandez *et alii*, 2004), the values of the dependent variable (Y_{calc}) results from

$$Y_{calc} = Y_0 + b_1X_1 + b_2X_2 + \cdots + b_nX_n$$

that is the linear combination of the recorded independent variables (X_n) weighted by the calculated (b_n) regression coefficients (Table 4). Results showed that considered environmental variables for MLR analysis predicted 15% and 6% (R = 0.386 and R = 0.24) of the changes observed in CO_2 flux and H_2 molar fraction, respectively. The normalized residuals of the MLR analysis, reported on the time-series for both the H_2 and CO_2 (Figure-4a and -4b), showed that H_2 pulses and long-

TABLE 4

Summary of the multiple linear regression analysis (MLR) on the observed H_2 molar fraction, CO_2 flux, Air temperature, Atmospheric pressure, Wind speed and Wind direction. Environmental variables dataset was retrieved from Inguaggiato *et alii* (2020 and reference therein).

	Coefficient	**Standard Error**	**t-test**	**p-level**
Dependent variable = CO_2 flux; **Data no.** = 4838				
Intercept	96880	6574.32	14.74	0.00
Air temp	65.21	4.08	15.98	0.00
Atm Pressure	-98.78	7.24	-13.65	0.00
Wind direction	-0.25	0.27	-0.90	0.04
Wind speed	-168.60	7.14	-23.62	0.00
Dependent variable = H_2 molar fraction; **Data no.** = 6121				
Intercept	2475	175.97	14.07	0.00
Air temp	0.64	0.11	5.87	0.00
Atm Pressure	-2.67	0.19	-13.78	0.00
Wind direction	0.04	0.01	5.57	0.00
Wind speed	1.65	0.20	8.28	0.00

term variations of both H_2 and CO_2 cannot be dependent on changes in the environmental variables.

Fast Fourier Transform analysis (FFT) and filtering method

The Fast Fourier transform analysis (FFT) was the second processing method for both H_2 and CO_2. Data processing occurred to filter some cyclic variations that were independent of the volcanic activity. The FFT results allowed identifying a 1 cycle per day (cpd) frequency of variations (Fig. 5) that correlated with diurnal changes (24 hours) of atmospheric temperature and pressure. The correlation between soil CO_2 flux and air temperature on a daily time scale has widely been discussed in the literature (Maljanen *et alii*, 2002; Nakadai *et alii*, 2002). Diurnal variations were also observed in the time-series of CO_2 flux from mofettes and CO_2 concentrations in the West Bohemia region (Faber *et alii*, 2009; Weinlich *et alii*, 2006); in this case, the authors related the diurnal variations to the Earth's tides.

A specifically designed digital filter (band-stop frequencies $1.20 \cdot 10^{-5}$ – $1.11 \cdot 10^{-5}$ Hz; passband frequencies $1.26 \cdot 10^{-5}$ – $1.06 \cdot 10^{-5}$ Hz) allowed reducing the effects of cyclic variations. The filtering procedure enabled smoothing signals on the raw data (Fig. 6) and the results of the data processing were used for modelling purposes.

The FFT of the H_2 molar fraction dataset revealed variations having 1 cpd frequency (24 hours). Several authors noted similar cyclic changes in H_2 that were independent on the eruptive activity of different volcanoes (Sato & Mcgee, 1973; Di Martino *et alii*, 2013). These changes correlated with fluctuation of either air pressure and temperature. The above-described filtering procedure allowed removing these variations. The results of the filtering procedure were graphically reported as a smoothed curve on the observed H_2 time-series and used in the following data modelling.

Classification of the ground gas emissions

The comparison of the FFT and MLR results showed a high correlation between filtered signals and residuals ($R^2 = 0.753$ and $R^2 = 0.745$ for CO_2 and H_2, respectively). This result proved the goodness of the adopted processing procedure by the FFT and digital signal processing method.

The probability plot (Sinclair, 1974) provided the classification of the filtered CO_2 flux dataset. The statistical graphic approach of Sinclair (1974) enables classifications of log-normal scattered dataset, each population producing

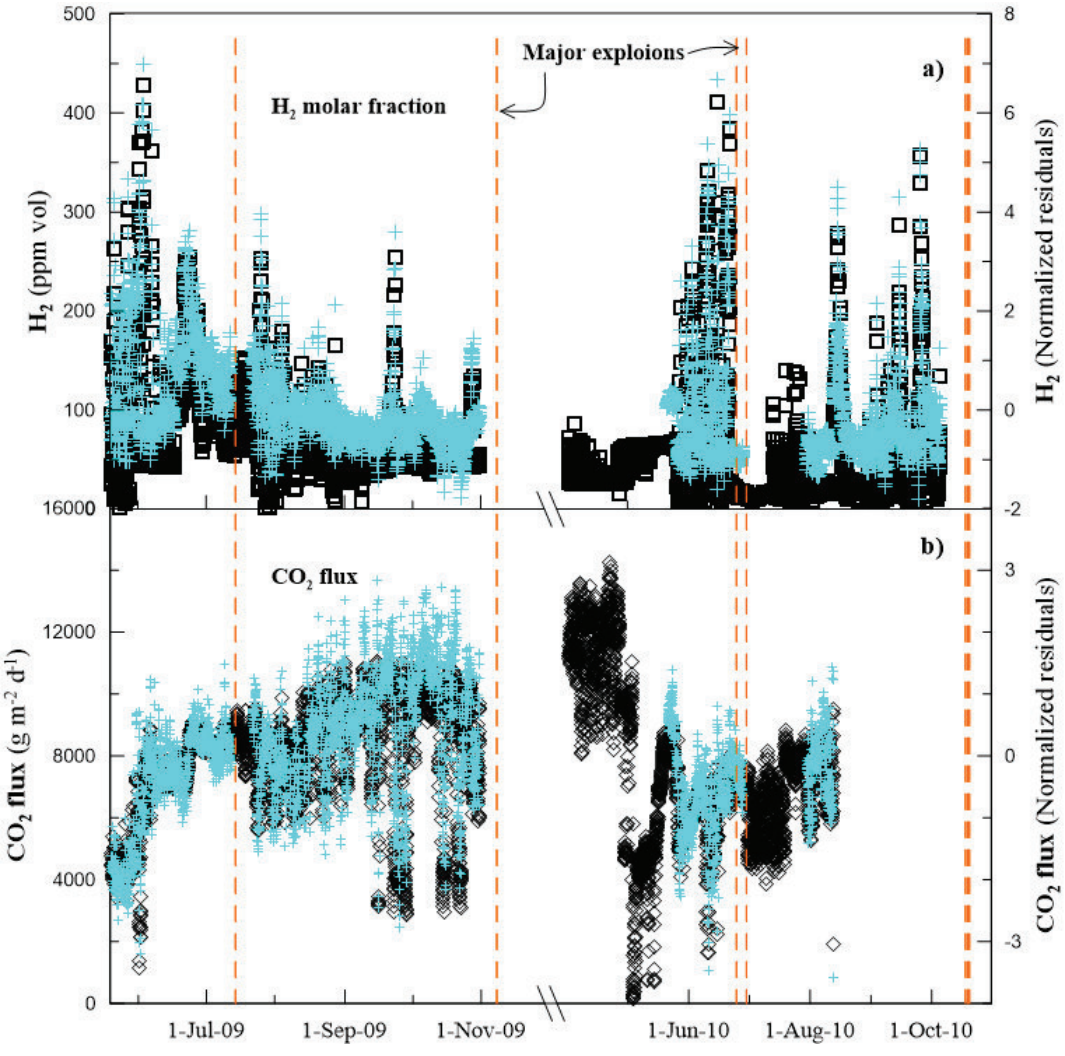

Fig. 4 - Time-series of the H_2 molar fraction and CO_2 flux measurements. The residuals of multiple linear regression analysis (MLR) are reported on the row dataset (ice blue crosses).

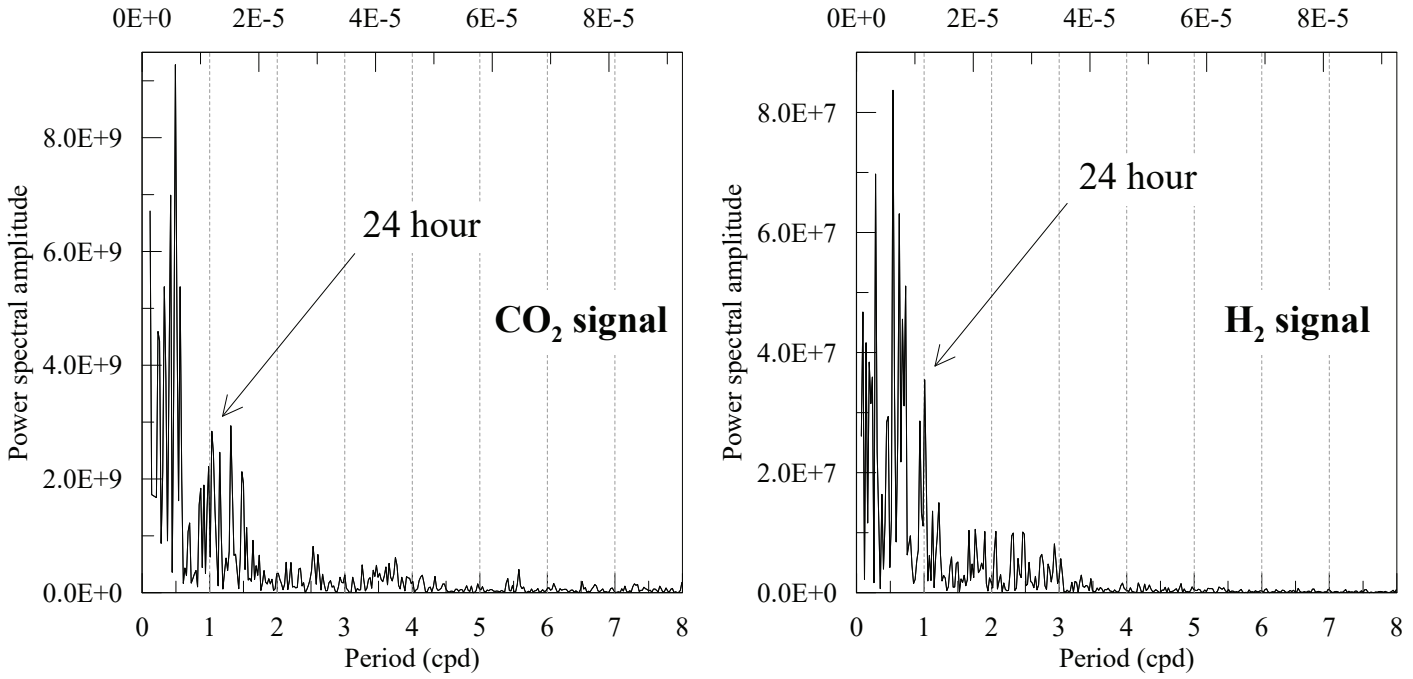

Fig. 5 - a) Power spectral density (PWD) of the CO_2 flux signal. b) Power spectral density (PWD) of the H_2 molar fraction signal. Sampling frequency 1 hour. Arrows show the sampling frequency corresponding to 1 cycle per day (cpd).

a straight line in the probability graph. The inflection points of the distribution divide different subsets. The cumulative probability of the CO_2 flux can be modelled through four subsets (Fig. 7a). The classification statistics (Table 5) shows that ordinary subset (i.e. "background population" according to Sinclair's notation) encloses the cumulative 44.5 % of the dataset (CO_2 flux range 3980 – 7893 g m^{-2} d^{-1}), while 51.8 % refers to anomalous CO_2 flux (range 7894 – 14251 g m^{-2} d^{-1}). Both the low and the very low CO_2 flux subsets (range 207 – 3979 g m^{-2} d^{-1} and 101 – 204 g m^{-2} d^{-1}, respectively) are the cumulative 3.7%. They account for sharp drop in ground permeability and thus, decrease of CO_2 flux (Camarda *et alii*, 2017).

The classification based on the probability method allows identifying four subsets of H_2 molar fractions. Each subset correlated with different level of the time changing explosive activity of Stromboli (Fig. 7b). Besides low H_2 subset (0.1 % cumulative probability) accounting for sensor accuracy in the measurements of H_2 in air (0.5 ± 5 ppm vol), the relevant part of the full dataset (92.23 cumulative %) encloses the ordinary subset (range 8 – 125 ppm vol; average 35 ppm vol). In contrast to the trends showed in the CO_2 flux time-series, sudden variations marked the time-series of H_2 concentration (Fig. 3b). These pulses were sudden changes of H_2 molar fraction in the range of either anomalous (6.8 cumulative %; H_2 concentration range 126 – 250 ppm vol) or very anomalous values (0.85 cumulative %; H_2 concentration range 252 – 428 ppm vol). According to several authors, some pulses of H_2 molar fraction marked important changes in the eruptive activity

TABLE 5

Statistics of the dataset classification based on the probability distribution (Sinclair,1974). The 50% cum are the H_2 concentration and CO_2 flux values relative to 50% of the cumulative probability of each subset that is identified in the probability plot.

Dataset	**Subset**	**Cumulative %**	**Min.** (ppm vol)	**Max.** (ppm vol)	**Average (50% cum)** (ppm vol)
H_2	Very Anomalous	0.85	252	428	309
	Anomalous	6.82	126	250	158
	Ordinary	92.23	8	125	33
	Low	0.10	0.9	8	3
			Min. (g m^{-2} d^{-1})	**Max** (g m^{-2} d^{-1})	**Average (50% cum)** (g m^{-2} d^{-1})
CO_2	Anomalous	51.80	7894	14251	9120
	Ordinary	44.50	3980	7893	4467
	Low	3.57	207	3979	1259
	Very Low	0.13	101	204	166

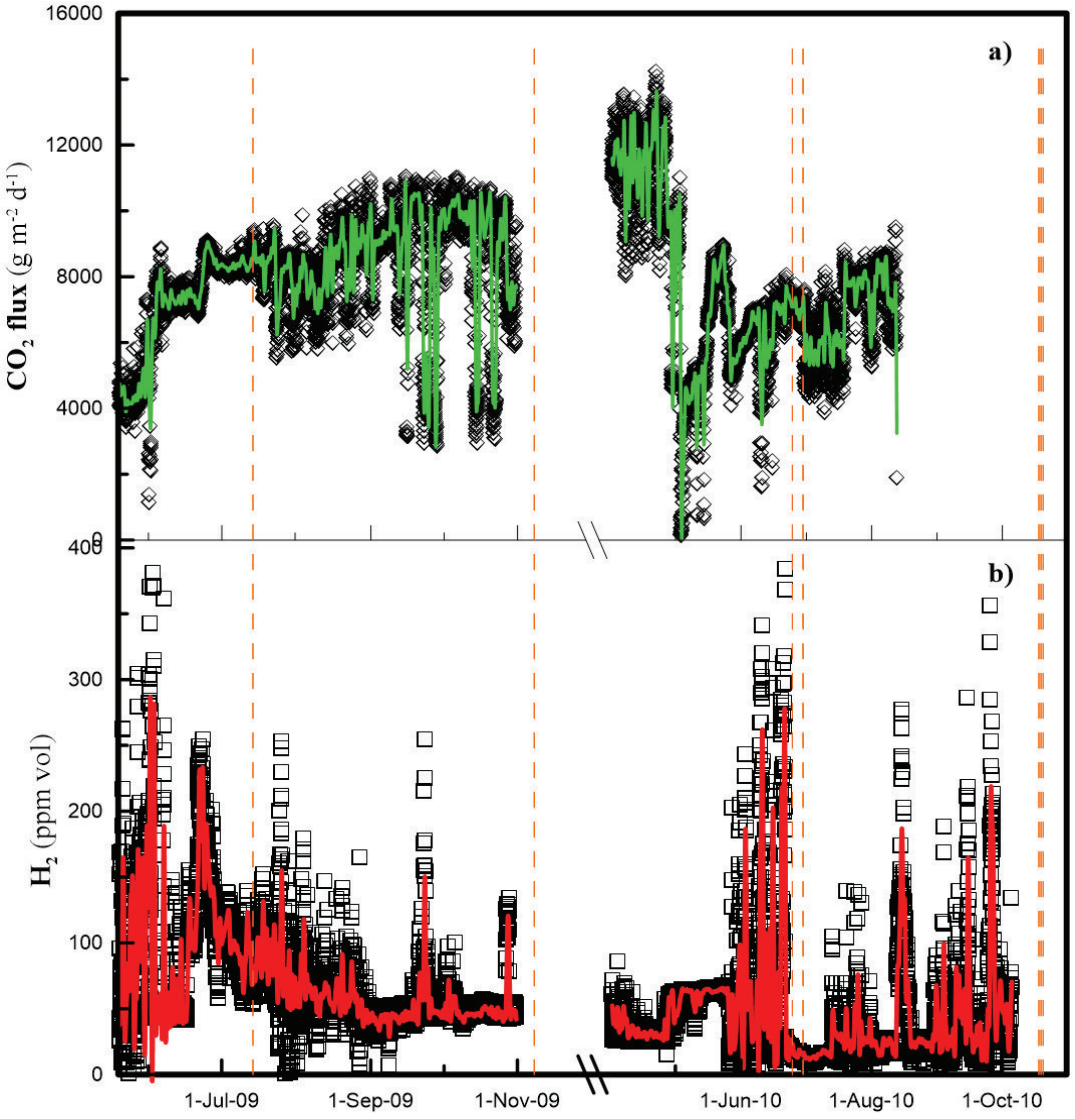

Fig. 6 - a) Time-series of the CO_2 flux measurements. Filtered data (green line) are superimposed to the row dataset of hourly measurements. b) Time-series of the H_2 molar fraction measurements. Filtered data (red line) are superimposed to the row dataset of hourly measurements. Major explosion events are shown (vertical dashed lines).

of different volcanoes (Sato & McGee, 1973; Carapezza & Federico, 2000; Carapezza *et alii*, 2004; Di Martino *et alii*, 2013; Di Martino *et alii*, 2016a).

DISCUSSION

The H_2 pulses were changes in the H_2 molar fraction from ordinary values (< 125 ppm vol) to either anomalous (126 – 250 ppm vol) or very anomalous ranges (> 252 ppm vol). Previous studies surveyed continuously the H_2 molar fraction at Stromboli for a few hours, during a period of intense strombolian activity (Carapezza & Federico, 2000). They found short living fluctuations (a few minutes) correlated with strombolian explosions.

The changes observed in the H_2 molar fraction accounted for fluctuations of the oxygen fugacity (fo_2) of the fumarolic gas near the condition of redox equilibrium. Water release during magma ascent produces dramatic changes in magmatic fo_2 because of H_2 diffuses a million times faster than O_2 (Chaermichael & Ghiorso, 1986; Giggenbach, 1987; Nuccio & Valenza, 1998; Kelley *et alii*, 2009). Dissociation of magmatic water at high temperatures releases H_2 in volcanic gases. The gas-melt-crystal reactions hamper significant deviations from redox equilibrium by partitioning sulphur, iron, and other components sensible to the redox state among melt, gas and crystal phases. Therefore, the H_2 pulses in the volcanic gases account for transient increases in oxygen fugacity (Sato & Wright, 1966; Sato, 1972; Sato & Valenza, 1980; Valenza & Nuccio, 1998).

A near-continuous injection of gas-rich magma from depth (LP-magma) sustains both the gas emissions and ejection of porphyric scoriae (HP-magma). According to Métrich *et alii* (2010), the transition to HP-magma implies dehydration of LP-magma in the shallow plumbing system of Stromboli. Thus, the water loss promotes H_2 formation, because of fluctuations near the equilibrium:

$$H_2S + 2\,H_2O \leftrightarrows SO_2 + 3\,H_2 \qquad [1]$$

which includes the main sulphur species, water, and hydrogen in the gas phase. The fast-responding equilibrium between sulphur species (Equation 1) shifts to the right when the magma degassing occurs at shallow depth (Delmelle & Stix, 2000). That equilibrium is controlled by:

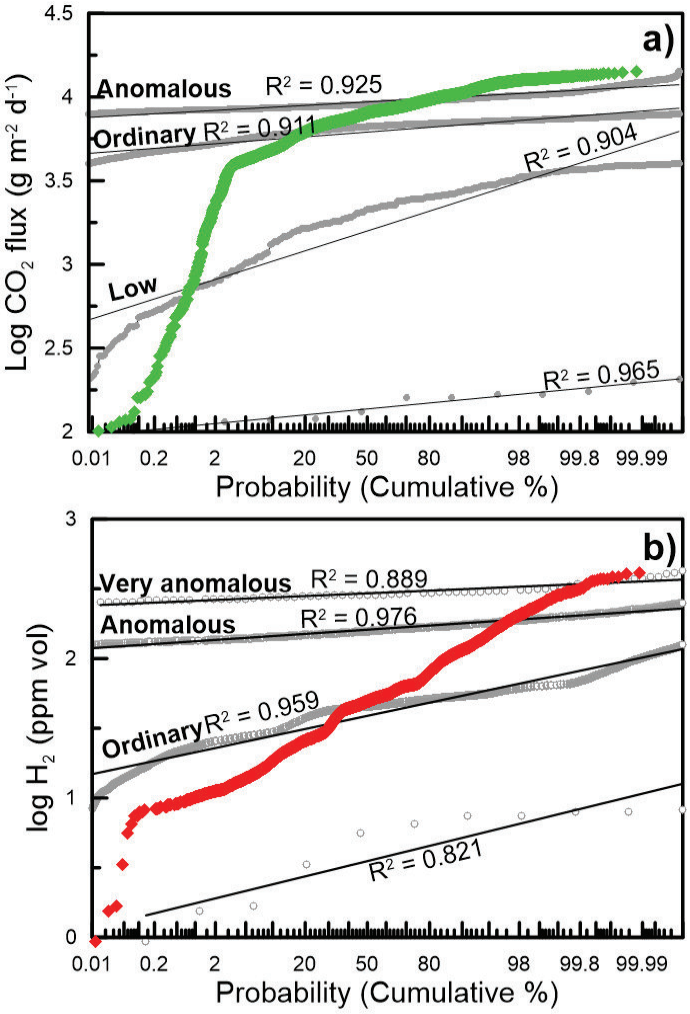

Fig. 7 - a) Log probability plot for CO_2 flux dataset. b) Log probability plot for H_2 dataset.

$$log\frac{SO_2}{H_2S} = +2logH_2O + \log K_{eq} - 3\log H_2 \quad [2]$$

where K_{eq} is the equilibrium constant (Giggenbach, 1987). Equation (2) shows that changes in the SO_2/H_2S ratio have a strong effect on H_2. Therefore, significant shifts in H_2 molar fraction can be sensitive tracers of the changes in the sulphur speciation (i.e. increases in the f_{H_2S}). Notably, the increases in the f_{H_2S} suggests a high degassing pressure (Delmelle & Stix, 2000). Recently, Métrich *et alii* (2010) showed that sulphur partitioning in the gas phase occurs in the intermediate/shallow plumbing system of Stromboli (4 – 2 km). There, the dehydration originates HP-magma and shifts gases towards a more reducing state. Therefore, the decrease in f_{O_2} promotes sulphur dissolution as an immiscible sulfide. As expected, SO_2/H_2S ratio does not change significantly (Aiuppa *et alii*, 2005), since the H_2 loss promotes oxidation of H_2S to SO_2.

Characterization of H_2 and CO_2 related to major explosions

An attempt to identify the magmatic gas release, promoting shifts in the H_2 molar fraction and CO_2 flux, included correlation with the major explosions. Throughout the 2009 – 2010, four events of very anomalous H_2 molar faction preceded five major explosions (Fig. 6). Besides, three of them occurred during periods of high CO_2 flux from the ground.

Correlation between observations and the eruptive events based on the binomial test. This approach enabled correlating significant changes in either CO_2 flux or groundwater chemistry to seismic events (Skelton *et alii*, 2014; Camarda *et alii*, 2016; Tamburello *et alii*, 2018). The binomial test allowed evaluating the correlation likelihood of specific events in contrast with the null hypothesis (no correlation). Calculation of the P-values was computed according to:

$$P = \frac{p^n(1-p)^{(N-n)}N!}{n!(N-n)!} \quad [2]$$

where p is the probability that shifts in H_2 (or CO_2) occurred randomly over the time window of monitoring (1/360 days = 2.78 x 10^{-3}), p^n is the correlation probability of each H_2 peak and the specific major explosion, n is the number of positive events (major explosions) which occurred in the arbitrary time window (i.e. 4, 8, 9, 11, 16, 21, 38, 43, 50, 60, 85, 100 days), and N is the number of major explosions that occurred throughout 2009 – 2010. Changes in either H_2 or CO_2 are independent of explosive events for $P > 0.05$.

Calculation of the P-values included all potential shifts in the very anomalous range of H_2 and anomalous range of CO_2 (Figs. 8a and 8b) occurring before the specific major explosions and allowed excluding the independent events ($P > 0.05$). The P-values showed the highest correlation likelihood for H_2 pulses occurring 240 – 720 hours before the major explosions. P-values calculated for CO_2 (Fig. 8b) were comparable with those of H_2, although concurrent measurements of H_2 molar fraction and CO_2 flux showed a low correlation ($R^2 = 0.03$). Thus, CO_2 flux and H_2 molar fraction probed independently the strombolian eruptions. As expected, the widest time window (100 days) showed the highest P-values, although the null hypothesis cannot be accepted. The calculation of the P-values showed that major explosions occurred often 10 - 30 days after very anomalous H_2 pulses, although some correlated events occurred after ~100 days (2400 hours). Several authors noted comparable time windows in the dynamics involving the plumbing system of Stromboli. For instance, significant changes in the seismic signals preceded from several weeks to months the major explosive events (Falsaperla & Spampinato, 2003). Further, remarkable changes in $^3He/^4He$ ratio dissolved in groundwater (Inguaggiato & Rizzo, 2004; Capasso *et alii*, 2005; Carapezza *et alii*, 2009; Rizzo *et alii*, 2015), increases of partial pressure of CO_2 dissolved in groundwater (De Gregorio *et alii*, 2007; Inguaggiato *et alii*, 2017a), and shifts in the gas emissions from the ground occurred several weeks to months before major changes in the volcanic activity of Stromboli.

Characterization of H_2 and CO_2 with the ordinary eruptive activity

Besides temperature and pressure, the redox state of the magma has a key role in the gas-melt partitioning of the multivalent elements (i.e. sulphur). The eruptive activity of Stromboli involves the average continuous injection of CO_2-rich LP-magma (Landi *et alii*, 2006). Crystallization

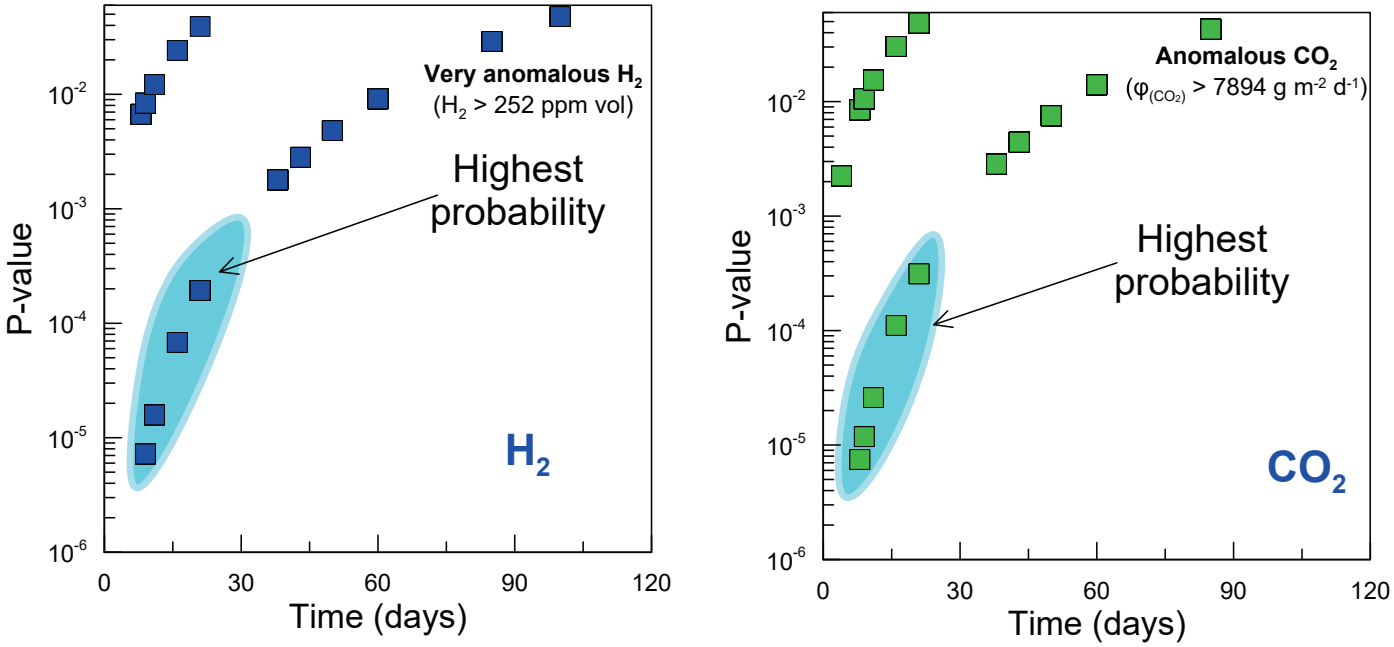

Fig. 8 - a) Results of the binomial test to assess the correlation between the major explosions and the very anomalous H_2 peaks. b) Results of the binomial test to assess the correlation between the major explosions and the anomalous CO_2 peaks. The blue area indicates the time window that shows the highest probability to observe major explosions after the change in H_2 concentration and CO_2 flux.

and dehydration (water loss) promote the transition to HP-magma in the shallow plumbing system (4 – 2 km). This transition affects sulphur speciation (i.e. changes in SO_2/H_2S ratio) and increases the reducing capacity of the volcanic gases. The H_2 molar fraction in the crater fumarole provided some information on the changes of the redox state in the shallow plumbing system.

The hourly average of VLP events allows distinguishing among different levels of the ordinary volcanic activity of Stromboli (Chouet *et alii*, 2003). Comparisons of CO_2 flux and seismic signals (VLP number and amplitude) showed correspondence between CO_2 flux anomalies and a high number of explosions (Carapezza *et alii*, 2009). The number of VLP events can also be a useful benchmark for H_2 signal. Fig. 9 shows the threshold values of both H_2 and CO_2 and the average number of VLP on an hourly basis. This comparison showed some changes in the gas emissions from the crater fumarole associated with changes in the eruptive activity. Some anomalies in H_2 molar fraction (range 125 – 250 ppm vol) occurred in 2009 when a high number of explosions were recorded (VLP > 12 events by hour, orange area in Fig. 9). The H_2 molar fraction was in the ordinary range (30 – 125 ppm vol) from September to November 2009, during periods of low-ordinary eruptive activity of Stromboli (VLP < 12 events per hour, green area in Fig. 9).

A close comparison with the average number of VLP events (Fig. 9) revealed that CO_2 flux tracked the explosivity of the volcanic eruption, rather than the frequency of the explosions. From July 2009 to August 2010, at least 3 over 5 major explosions occurred during periods of CO_2 flux emissions above the anomaly threshold. Recent studies found that continuous increases of CO_2 flux started a few months before the 2020 paroxysmal explosions, accounting for increased gas pressure in the plumbing system (Inguaggiato *et alii*, 2020). Furthermore, some changes in the VLP signals were attributed to higher gas content in the strombolian explosions, starting at least one month before the 3 July 2019 paroxysmal event (Giudicepietro *et alii*, 2020). Our results are consistent with the scenario of a magmatic released of CO_2 at high pressure (> 280 MPa). The HP-magma coexisted with a separated CO_2-rich gas feeding the ordinary explosions at Stromboli. Dehydration and water loss promoted H_2 pulses in the shallow part of the plumbing system. A comparison of the results reported in this paper with both models and data from literature would suggest that changes in the gas emissions heralded some changes in the eruptive activity of Stromboli.

CONCLUSIONS

Some major explosions punctuated the ordinary eruptive activity of Stromboli throughout the 2009 – 2010. During that period, we performed a continuous survey of CO_2 and H_2 in the volcanic gases. The results of this study allowed us to correlate the changes in volcanic gas emissions and persistent eruptive activity of the volcano.

Measurement collection of both CO_2 flux and H_2 molar fraction occurred hourly at crater fumaroles. The MLR and FFT analyses allowed filtering the effects correlated with changes in the environmental variables. The statistic approach also allowed us to identify two CO_2 flux subsets and three H_2 molar fraction subsets. This classification showed some changes in the gas emissions during the time window of monitoring that correlated with changes in the eruptive activity of Stromboli. The ordinary CO_2 flux (range 3980 – 7893 g m^{-2} d^{-1}) correlated with the ordinary eruptive activity of Stromboli. Our results confirmed that near-continuous injection of gas-rich LP-magma enables

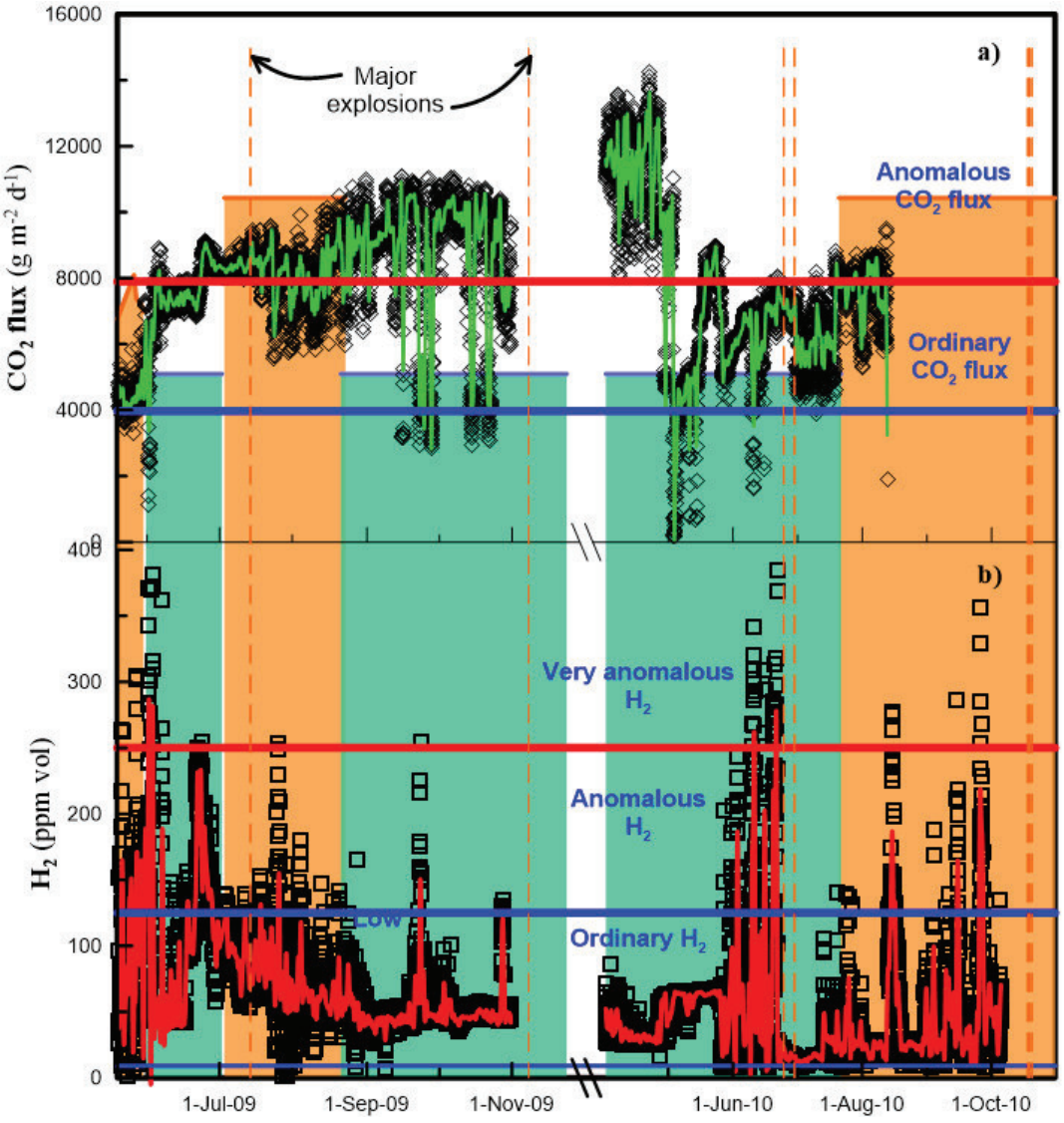

Fig. 9 - Time-series of H_2 and CO_2 in comparison to the ordinary eruptive activity of Stromboli; a) the statistical based threshold values of anomalous (red horizontal line) and ordinary (blue horizontal line) CO_2 flux emissions are shown as reference; b) the statistical based threshold values of very anomalous/anomalous (red horizontal line) and anomalous/ordinary (blue horizontal line) of H_2 concentration are shown as reference. Green area indicates low level of eruptive activity period (VLP < 12 events per hour); orange area indicates high level of eruptive activity period (VLP > 12 events per hour).

the persistent emissions of a gas plume from the craters, the gas emissions from the ground, and the strombolian explosions. The ascents of LP-magma batches occurred in near equilibrium with a separated CO_2-rich gas. Thus, the increases of the CO_2 flux accounted for an increased supply of the gas-rich LP-magma that refilled the shallow volcanic plumbing system (4 – 2 km).

Surveying of H_2 molar fraction pointed out changes in the reducing capacity of the volcanic gases during the period of monitoring. Besides pressure and temperature, this variable affects the gas-melt sulphur partition, resulting in a sensitive tracer of the SO_2/H_2S ratio. The transition to scoriaceous HP-magma occurs by dehydration of LP-magma, forcing an increase of f_{H_2S} and a decrease of f_{O_2}. According to several authors, the magmatic oxygen fugacity changes form NNO +1 to NNO –1 (Pichavant *et alii*, 2009) during this transition. The increased H_2O availability established favourable conditions to cause H_2 pulses. We stress here that sulphur inclusion in the gas phase can trigger the increases in the average explosive activity of Stromboli. The SO_2 addition in the gas phase can occur by H_2 loss and oxidation of H_2S.

The statistical classification allowed identifying some H_2 molar fraction subsets. The H_2 anomalies correlated with major explosions of the volcano. This correlation showed that short-term changes (lifetime 100 – 130 hours) from ordinary to the very anomalous values preceded the major explosions (650 to 400 hours). These results suggested that H_2 pulses coincided with changes in the eruptive activity of Stromboli by increases in either the number or in the size of explosions rather than a long-term precursory sign of major explosions.

This paper reported a long time-series of H_2 survey in volcanic gases and a characterization of the reducing capacity against the changes in the eruptive style of Stromboli. The H_2 data are currently available for a few volcanoes (i.e. Sato & Moore, 1973; Sato & McGee, 1982; Carapezza & Federico, 2000; Di Martino *et alii*, 2013). Therefore, further studies are necessary for an appropriate and more robust comparison to these results. However, this study showed some correlations between changes in the volcanic gas emissions and the eruptive activity of Stromboli. Thus, surveying H_2 molar fraction in volcanic gases can be an auxiliary parameter of the CO_2 flux in the volcanic surveillance programs.

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