Temporal analysis of $\delta^{13}C_{CO2}$ and CO_2 efflux in soil gas emissions at Mt. Etna: a new tool for volcano monitoring

Salvatore Giammanco[1,*], Bor Krajnc[2,3], Jože Kotnik[3], Nives Ogrinc[2,3]

[1] *Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania, Italy*
[2] *Jožef Stefan International Postgraduate School, Ljubljana, Slovenia*
[3] *Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana, Slovenia*

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ABSTRACT
We monitored the soil gas emission of CO_2 from selected sites of Mt. Etna volcano during the period February 2009 to December 2010 by measuring periodically the soil CO_2 efflux together with the associated stable carbon isotope composition of CO_2. Correlation between the two parameters showed distinct behaviors depending on the sites as a reflection of the different interactions between crustal and sub-crustal fluids. Where deep CO_2 interacted with shallow cold ground water and/or with shallow biogenic CO_2, a positive correlation between soil CO2 effluxes and carbon isotopes was evident and it depended strongly on the velocity of gas through the soil. In these cases, the highest CO_2 effluxes corresponded to $\delta^{13}C_{CO2}$ values similar to those of the deep magmatic CO_2 emitted from the crater and pericrateric gas emissions at the summit. In areas where a shallow hydrothermal system was presumed, then a similar correlation was less evident or even absent, suggesting strong control on C isotopes arising from the interactions between CO_2 gas and dissolved HCO_3- that occur in aquifers at T>120 °C. Marked temporal variations were observed in both parameters at all sites. No significant effect of meteorological parameters was found, so the observed changes were reasonably attributed to variations in volcanic activity of Mt. Etna. In particular, the variations were attributed to increased degassing of CO_2 from incoming new magma, possibly coupled with increased hydrothermal activity in at least some of the shallow aquifers of the volcano. The largest anomalies in the monitored parameters preceded the opening of the New Southeast Crater in late 2009 and therefore they could represent a key to unveiling the dynamics of the volcano.

1. Introduction

Mt. Etna volcano, one of the most active volcanoes in the world, is also known as a one of the main sources of magmatic CO_2. The total emission rate has been recently estimated at about 60,000 t·d^{-1} [Hernández et al. 2015]. Most of the release of CO_2 occurs through the active summit vents of the volcano, but a remarkable fraction of this gas (about 10 % of the total amount according to D'Alessandro et al. 1997b and Hernández et al. 2015] is released from its flanks. In this case, CO_2 emissions at the surface occur in diffuse form through volcano-tectonic faults [e.g., Giammanco et al. 1998, Aiuppa et al. 2004] and they are produced by magma outgassing from reservoirs located at intermediate to great depths beneath the volcano [Bruno et al. 2001, Aiuppa et al. 2004, Giammanco et al. 2013]. Studies on soil gas carried out in the last 17 years at Mt. Etna showed that the central eastern flank and the lower southwestern flank of the volcano are characterised by the strongest anomalies in both soil gas concentration and soil CO_2 efflux and by the highest content of magmatic CO_2, which dissolves into local groundwater [Anzà et al. 1989, Giammanco et al. 1995, 1996, Allard et al. 1997, Brusca et al. 2001, Aiuppa et al. 2004, Giammanco and Bonfanti 2009].

The aim of the present work was to study the temporal variations of soil CO_2 efflux and the associated stable carbon isotope composition of CO_2 over a time span of several months, covering the period between the end of the 2008-2009 flank eruption and the opening and eruption of the New Southeast Crater (NSEC), today the most active summit crater of Mt. Etna (Figure 1). The main objectives of our study are: i) to better define the correlation between the above two parameters in selected high-degassing sites of the volcano; ii) to model the dynamics of geochemical interactions between CO_2 and the surrounding environment and iii) to recognize possible influences of volcanic activity on soil degassing.

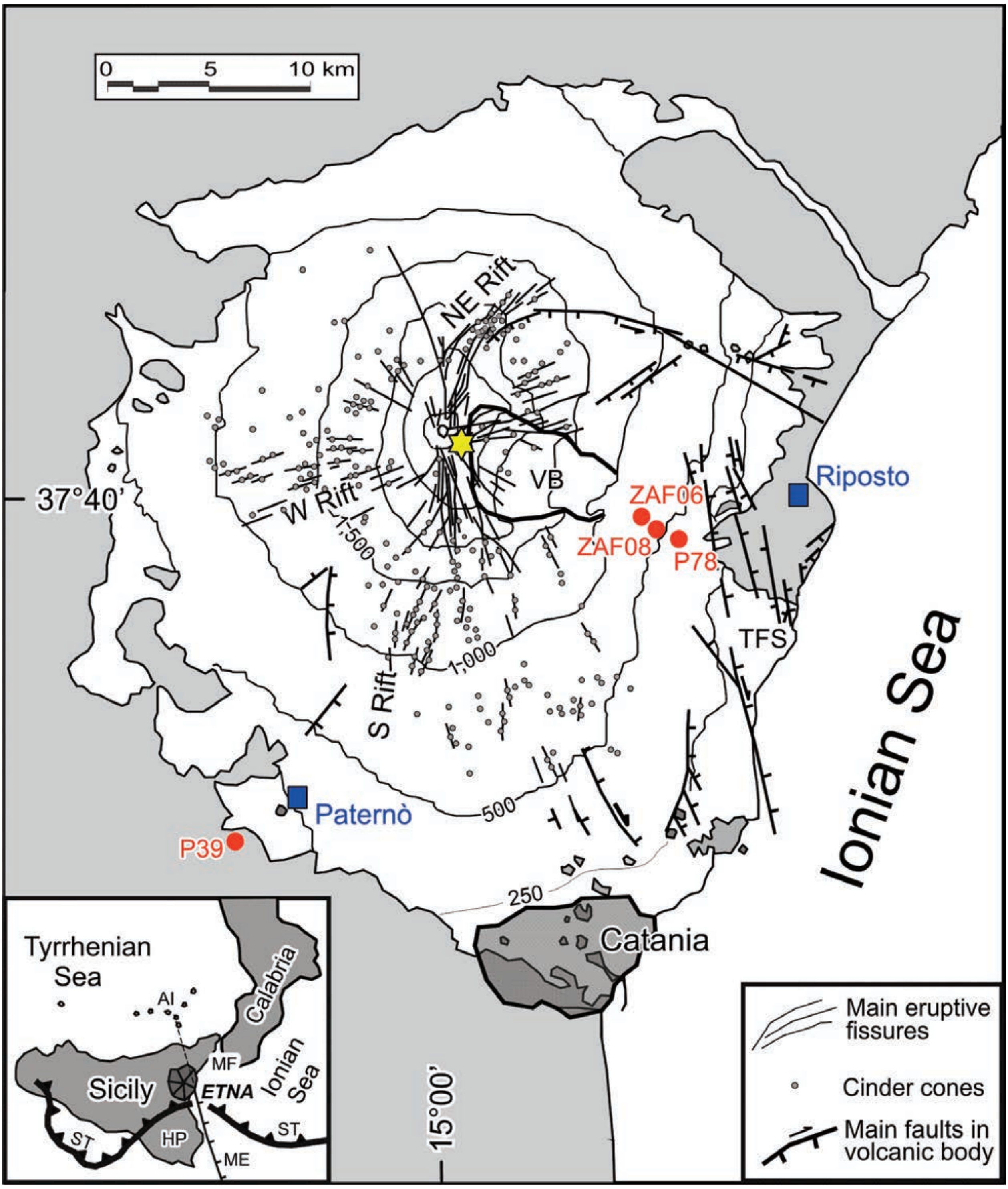

Figure 1. Map of the study area. The red circles indicate the location of soil CO_2 sampling points. The three main rift zones (NE, W and S) are also shown. VB = Valle del Bove morphological depression. The blue squares indicate the location of the two SIAS meteorological stations used for the purposes of this study. The yellow star shows the location both of the SE Crater and of the nearby NSEC.

2. Eruptive phenomena at Mt. Etna during the studied period

Mt. Etna is a large Quaternary composite volcano, which grew to its present elevation of 3320 m by accumulation of lavas and tephra erupted during the last 200 kyr [Gillot et al. 1994]. At present, its activity is represented by summit and/or flank eruptions, the former being mostly short-lived and characterized mainly by production of tephra with minor lavas, the latter being, on average, long-lived and mostly producing lava effusions that may emplace voluminous lava flow fields.

Our study began during the final stages of the long-standing 2008-2009 flank eruption. Details on this eruption are given in Bonaccorso et al. [2011] and in Corsaro and Miraglia [2014]. The eruption started on May 13th from a fissure that developed from the SE Crater towards the Valle del Bove (VB in Figure 1), a morphological depression that occupies a large part of the east flank of Mt. Etna. Lava flows from this fissure expanded inside the VB, reaching a maximum length of about 6 km and a total volume of about $70 \pm 20 \times 10^6$ m^3 [Branca S. quoted in Corsaro and Miraglia 2014]. The eruption ended on July 7th, 2009, 419 days after its onset.

Just a few months later, on November 6th, 2009, a new vent opened on the lower eastern slopes of the Southeast Crater, one of the four summit craters of Mt. Etna and the most active one in the last thirty years [e.g., Behncke et al. 2014]. This new vent, named New Southeast Crater (NSEC), appeared as a relatively small open pit emitting hot pressurised gas. Its birth marked the end of the eruptive activity at the SE Crater, thus virtually "replacing" it as a new opening in the conduit of the previous SE cone. The vigorous degassing activity of NSEC continued until the end of 2010, without appreciable changes.

In the meantime, since August 25th, 2010, some isolated explosive episodes occurred at the Bocca Nuova crater (BN), the westernmost of the four summit craters of Etna (for details on this and on the following volcanological information, see http://www.ct.ingv.it/en/rapporti.html).

The strong gas and ash explosion of August 25th, 2010 at the BN was followed by several smaller explosive events that produced short-lived emissions of volcanic ash. Seven major explosions occurred at BN until August, 29th, although with less intensity than the first one. Other significant explosive events took place at BN on October 7th and on November 1st, both producing minor ash plumes. After more than one month of relative quiescence at Etna, a new strong explosion occurred at BN on December 22nd, 2010. This explosion was probably less powerful than the one on August 25th, but certainly stronger than the numerous events between late August and November 2010.

On the afternoon of December 23rd, 2010, Strombolian activity apparently started for the first time inside the NSEC since its formation. However, bad weather conditions prevented clear observation of the summit area, so this activity could not be followed in detail. On the late afternoon of January 2nd, 2011 mild Strombolian activity appeared again within the pit of NSEC, preceded by several days of repeated emissions of hot gas. Strombolian explosions, although with variable intensity, continued through January 6th and then ceased. Mild explosive activity resumed on January 11th, and its intensity began to increase on January 12th until producing a small lava outflow. Finally, a paroxysmal eruption occurred during the night between January 12 and 13, with lava fountains and voluminous lava flows. The event ceased completely after about two hours. This was the first of a long and complex sequence of eruptive events that characterized the evolution and growth of the NSEC until 2015 [Behncke et al. 2014, De Beni et al. 2015].

3. Materials and methods

3.1. Sampling sites

For the purposes of this study, we selected the sites most representative of soil degassing (Figure 1), as they are all characterized by anomalous high emissions of soil CO_2. In particular, site P39 is located on the southwestern flank at an altitude of 115 m a.s.l., ~2 km SW of the town of Paternò, in an area with visible absence of vegetation due to the intense gas emissions from the soil. The other three sites (P78, ZAF06 and ZAF08) are located on the eastern flank of Mt. Etna, at altitudes between 320 m and 510 m a.s.l..

Apart from CO_2, the chemical composition of the gas released from all sites, but especially at P39, shows trace amounts of CH_4, He and sometimes H_2 and CO [Giammanco et al. 1998]. Previous geochemical studies on the gases emitted at sites P39 and P78 indicated that the origin of these gases is dominantly magmatic [D'Alessandro et al. 1997a, Giammanco et al. 1998, Pecoraino and Giammanco 2005]. In particular, the chemical and isotope features of gases emanating at site P39 show evidence of their direct origin from the mantle source of Mt. Etna basalts [Giammanco et al. 1998a, Caracausi et al. 2003a, 2003b]. This site is located on a NE-SW-directed regional fault that is thought, based mainly on geochemical data, to be part of the deep feeder system of Mt. Etna [>10 km; Caracausi et al. 2003a, 2003b]. Sites P78, ZAF06 and ZAF08 are part of an anomalous degassing zone that is aligned on a WNW-ESE fault system [Anzà et al. 1993, Giammanco et al. 1995]. A recent study on soil CO_2 emissions in the central eastern flank of Mt. Etna [Giammanco and Bonfanti 2009], recognized this line as a major fault characterized by clear anomalous degassing whose changes in time are linked to volcanic activity. Gases from this site are assumed to derive from a shallower portion (5 - 10 km) of the magma feeder system of Mt. Etna [Giammanco et al. 1998, Bruno et al. 2001].

3.2. Soil CO_2 efflux

Soil CO_2 effluxes (expressed in g m^{-2} d^{-1}) were measured at all selected sampling sites using the method of the dynamic accumulation chamber [e.g., Parkinson 1981, Chiodini et al. 1998, Farrar et al. 1995]. CO_2 effluxes were measured in at least duplicate during each survey, and the arithmetic average of the values was considered for the temporal analysis of data. The sampling frequency was variable but, on average, once every 20-30 days. The data cover the period from February 2nd, 2009 to December 12th, 2010. In order to evaluate the possible influence of the main meteorological parameters on the temporal variations of CO_2 efflux, values of air temperature, total daily rainfall, minimum and maximum relative humidity and wind speed at a height of 2 m above the ground were also acquired thanks to the monitoring network of the Servizio Informativo Agrometeorologico Siciliano (SIAS). In particular, we chose the station of Paternò, representative of the weather conditions of the low SW flank of Mt. Etna, and the station of Riposto, representative of the weather conditions of the low E flank of Mt. Etna (see Figure 1).

Because the CO_2 efflux data are log-normally distributed [Ahrens 1954, Giammanco et al. 2010], all graphic analyses of these data in the present paper have been performed on a $\log_{10}$ scale.

3.3. Stable carbon isotope composition of CO_2

Samples for stable isotope analysis were collected in the soil at a depth of 50 cm using a 5 mm ID teflon tube connected to a syringe. The gas aliquots were immediately injected into pre-evacuated 12-ml glass serum vials through a double-holed needle. To avoid possible contamination with gas from the sampler tube, the system was purged twice with the soil gas. The septum penetration needle allows direct delivery of the gas sample into the pre-evacuated vial thereby minimizing possible contamination with atmospheric air [Torn et al. 2003]. The stable isotope composition of CO_2 was determined according to the methods of Knohl et al. [2004] and Spötl [2004]. These methods have been applied successfully in various forest soils in Slovenia [Čater and Ogrinc 2011, Krajnc et al. 2016, Krajnc et al. 2017]. Measurements were made directly from vials using a Europa Scientific 20-20 continuous flow isotope ratio mass spectrometer (IRMS) coupled to an ANCA-TG preparation module for gas samples. Stable isotope results are reported using the conventional delta-notation ($\delta^{13}C_{CO2}$), in per mil (‰) relative to the VPDB reference standard - $\delta^{13}C_{CO2}$. The accuracy of the measurements was checked using "CO_2 ISO-TOP, High" CO_2 standard with $\delta^{13}C_{CO2}$ value of -4.3 ± 0.2‰. The precision of measurements was ± 0.2‰.

4. Results and discussion

4.1. Geochemical characterization of sites

The results of the measurements carried out during our study are shown in Table 1. Figure 2 shows the correlation plot between the $\delta^{13}C_{CO2}$ values and the corresponding $\log_{10}$ values of CO_2 efflux measured at all sites. Site P39 displays the highest levels of CO_2 efflux (up to about 32,000 g m^{-2} d^{-1}) and the most positive values of $\delta^{13}C_{CO2}$ (between +1.6 and +3.1‰). Furthermore, the isotope composition of carbon showed very small variation with time, despite the wide range of CO_2 effluxes measured. This is in line with previous measurements of both parameters at this site [Giammanco et al. 1998, Pecoraino and Giammanco 2005]. The isotopic shift of carbon observed at this site was explained as being due to strong interaction between deep magmatic fluids and a hydrothermal aquifer at T° > 120 °C because, in this case, the fractionation factor in water between gaseous CO_2 and dissolved HCO_3^- favors enrichment of the heavier carbon isotope in the residual gas phase that passes through the ground water [Mook et al. 1974]. Higher water temperature causes a larger positive isotopic shift in $\delta^{13}C_{CO2}$ values. In fact, the presence of a geothermal aquifer beneath the area of Paternò has already been postulated by Chiodini et al. [1996], who calculated a temperature of water of up to about 150 °C, based on liquid and gaseous geothermometers. In our case, the deep CO_2 that interacts with the hydrothermal aquifer at about 150 °C should undergo an isotopic shift of about +2‰ [Mook et al. 1974]. Therefore, the estimated $\delta^{13}C_{CO2}$ values of the pristine deep CO_2 before interaction with thermal water would be very similar to those measured in the high-temperature fumaroles near the summit of Mt. Etna [Giammanco et al. 1998, Aiuppa et al. 2004], assumed as representative of the C-isotope composition of magmatic CO_2 of this volcano (grey horizontal band in Figure 2). However, the C isotope values found in this study at site P39 are slightly more positive than those found at the same site in previous work [Giammanco et al. 1998, Pecoraino and Giammanco 2005]. If we assume a pristine C-isotope composition in the range from -2.5 to -1‰ as representative of the magmatic CO_2 emitted from Etna [Giammanco et al. 1998, Pecoraino and Giammanco 2005], then the range of values that we observed would be compatible with an isotopic shift of +3 to +4‰. According to Mook et al. [1974], such a fractionation factor would be due to interaction between CO_2 and the hydrothermal system at a water temperature of 180-200 °C. A summary of the above geochemical interactions for site P39 is shown in the graphic model of Figure 3a.

The other monitored sites showed a distinct and generally coherent behavior. Figure 2 highlights that, differently from site P39, $\delta^{13}C_{CO2}$ values at sites P78, ZAF06 and ZAF08 showed a wider range of variations

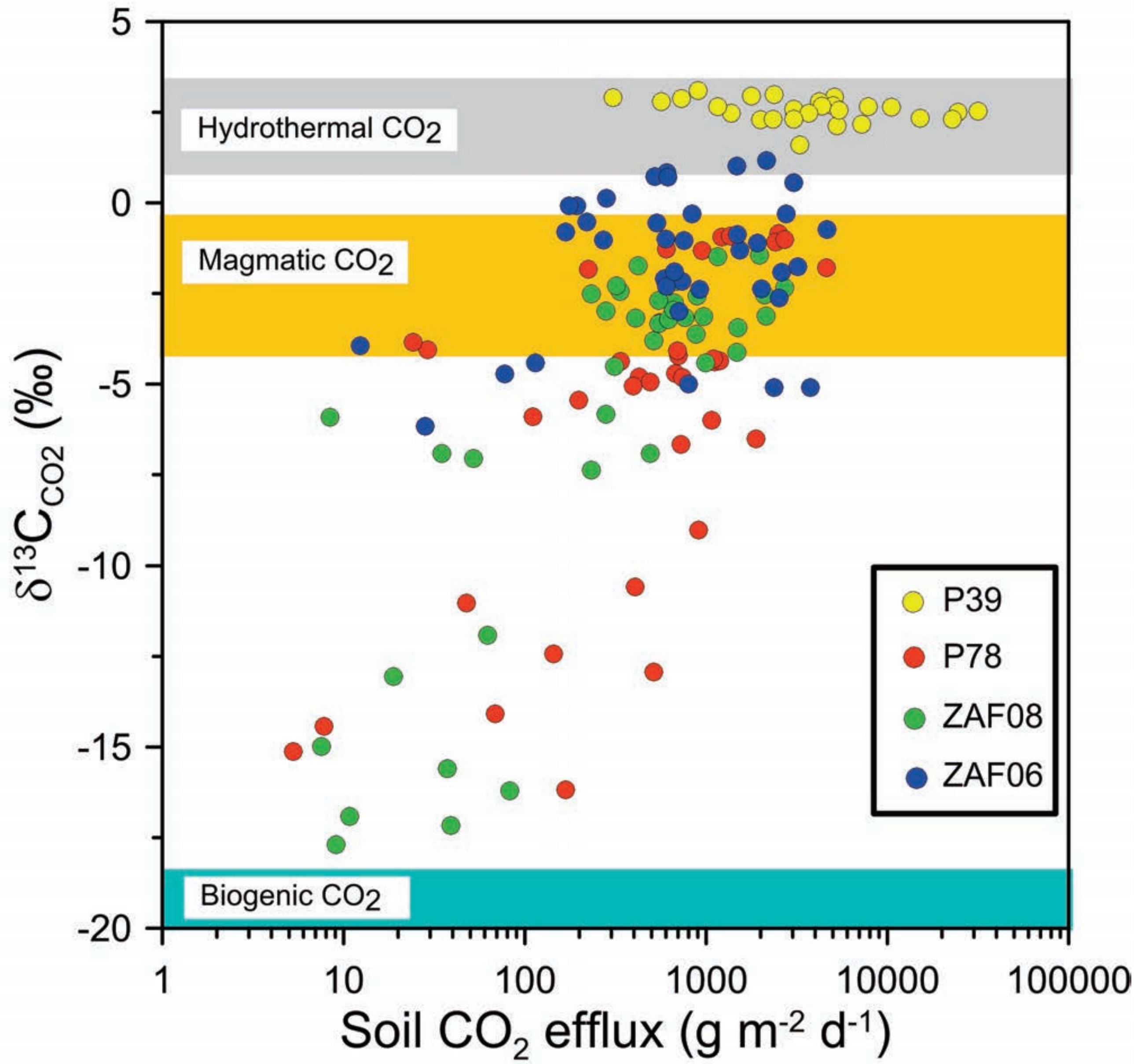

Figure 2. Correlation plot between $\delta^{13}C_{CO2}$ values and the corresponding log10 values of CO_2 efflux measured at all sites. The horizontal bands indicate the ranges of $\delta^{13}C_{CO2}$ values related to the main sources of CO_2 found at Mt. Etna (i.e., biogenic, magmatic and hydrothermal).

with time (from about -18‰ to about +1‰), although with a smaller deviation (from about -6‰ to about +1‰) at site ZAF06. The most negative $\delta^{13}C_{CO2}$ value clearly points to a marked influence of an organic component in the emitted CO_2, produced from a shallow biogenic source of gas in the thick and well-structured soil in these sites [e.g., Giammanco et al. 1998]. It must be considered, however, that a shift towards more negative values of $\delta^{13}C_{CO2}$ may also occur as consequence of fractionation of C-isotopes between gaseous CO_2 and dissolved HCO_3^- when deep CO_2 reacts with cold ground water for a long time. The eastern flank of Mt. Etna is characterized by the ubiquitous presence of large unconfined aquifers. Therefore, deep CO_2 rising at high pressure (>> 100 kPa) through faults inevitably encounters ground water and at least in part reacts with it, both chemically and isotopically. The entity of these reactions is more or less marked as a function of the contact time between gas and water. A long reaction time occurs because of long pathways of CO_2 gas through a thick aquifer or more generally because of low gas flux conditions. Given enough contact time between high-pressure dissolved CO_2 and water, the fractionation factor ranges from -9.6 to -8.5‰ in the temperature interval between 10° and 25°C [Mook et al. 1974]. The above geochemical interactions for sites ZAF06, ZAF08 and P78 are summarized in the graphic model of Figure 3b. The slightly more positive values observed at site ZAF06 may be due at least to partial interaction between deep magmatic CO_2 and thermal ground water, similar to that observed at site P39. It should be noted that this site is located very close to a water well ("Petrulli" well) with

Date	ZAF06		ZAF08		P78		T_{air}	Rain	RH min	RH max	Wind
	CO_2 flux	$\delta^{13}C_{CO2}$	CO_2 flux	$\delta^{13}C_{CO2}$	CO_2 flux	$\delta^{13}C_{CO2}$	°C	mm	%	%	m/s
02/03/09	3753	-5.10	233	-7.37	514	-12.93	14.70	0.00	55.00	100.00	1.09
02/16/09	12.4	-3.94	9.10	-17.69	5.30	-15.12	7.87	0.00	33.00	72.00	0.88
02/26/09	28.2	-6.17	7.60	-14.98	7.80	-14.43	9.20	0.20	30.00	73.00	1.95
03/12/09	77.5	-4.72	82.3	-16.21	68.5	-14.08	12.06	0.00	31.00	92.00	3.21
03/24/09	115	-4.42	39.1	-17.17	169	-16.18	10.96	0.00	38.00	79.00	0.98
04/09/09	2369	-5.10	62.3	-11.92	47.8	-11.03	13.23	2.80	66.00	100.00	0.53
04/20/09	n.d.	n.d.	493	-6.92	406	-10.58	14.38	9.00	78.00	100.00	0.69
04/29/09	798	-5.00	280	-5.83	145	-12.43	15.98	0.00	39.00	98.00	0.75
05/13/09	709	-3.00	1480	-4.13	909	-9.02	18.22	0.00	40.00	92.00	0.87
06/01/09	587	-2.10	882	-3.62	1075	-6.00	21.14	0.00	64.00	100.00	0.80
06/15/09	2534	-2.62	548	-3.34	676	n.d.	23.69	0.00	27.00	69.00	0.89
06/26/09	1212	n.d.	515	-3.81	427	-4.80	21.80	0.00	41.00	79.00	0.81
07/13/09	2017	-2.37	991	-4.41	856	n.d.	24.00	0.00	37.00	84.00	0.98
07/30/09	920	-2.39	968	-3.14	1118	-4.39	26.46	0.00	34.00	78.00	0.97
08/10/09	736	-2.16	1493	-3.44	1188	-4.36	25.95	0.00	52.00	94.00	0.74
08/25/09	603	-2.31	764	-3.16	1104	-4.31	26.07	0.00	55.00	100.00	0.65
09/07/09	667	-1.90	619	-3.22	702	-4.22	23.46	6.40	38.00	100.00	1.17
10/22/09	2604	-1.91	2138	-3.12	1887	-6.52	20.15	8.00	83.00	100.00	0.42
11/01/09	1921	-1.11	232	-2.52	491	-4.95	13.53	0.00	43.00	82.00	0.77
11/16/09	757	-1.04	2104	-2.54	396	-5.06	17.65	0.00	25.00	74.00	0.80
12/10/09	534	-0.55	52.2	-7.06	338	-4.37	13.13	0.00	39.00	76.00	2.88
12/30/09	601	-1.00	2722	-2.35	678	-4.71	15.34	0.00	48.00	89.00	0.64
01/19/10	272	-1.03	37.3	-15.60	198	-5.44	9.99	1.60	42.00	100.00	1.20
01/29/10	3200	-1.76	408	-3.18	727	-6.67	9.51	0.00	59.00	90.00	0.68
02/12/10	193	-0.08	10.8	-16.91	29.0	-4.05	9.19	0.00	16.00	100.00	2.49
03/01/10	1540	-1.31	895	-2.57	740	-4.82	14.53	0.00	52.00	100.00	0.63
03/19/10	220	-0.53	18.8	-13.05	111	-5.90	11.28	0.00	40.00	81.00	1.05
04/09/10	1487	-0.87	336	-2.45	697	-4.09	14.10	0.00	50.00	85.00	0.56
04/26/10	4638	-0.74	670	-2.77	556	-3.31	16.83	0.00	55.00	100.00	0.72
06/08/10	2158	1.16	661	-2.96	949	-1.32	21.25	0.00	42.00	100.00	0.48
06/22/10	1479	1.01	312	-4.52	1223	-0.94	19.87	0.00	43.00	100.00	0.15
07/14/10	608	0.83	685	-2.16	2506	-0.85	25.93	0.00	48.00	100.00	0.93
07/29/10	521	0.72	422	-1.74	1362	-0.92	23.98	0.00	53.00	83.00	0.90
08/26/10	614	0.71	1156	-1.49	2415	-1.08	26.45	0.00	44.00	100.00	0.78
09/09/10	3037	0.55	550	-2.69	2723	-1.02	23.68	104.20	53.00	100.00	1.09
09/23/10	281	0.13	321	-2.29	605	-1.28	20.33	0.40	61.00	100.00	0.57
10/06/10	2777	-0.30	1971	-1.45	4606	-1.79	21.67	0.00	72.00	100.00	0.59
10/22/10	838	-0.30	8.40	-5.91	24.2	-3.85	16.95	0.80	75.00	100.00	0.75
11/19/10	176	-0.08	34.9	-6.92	224	-1.83	14.74	0.00	52.00	95.00	0.76
12/07/10	167	-0.80	281	-2.98	709	-3.04	13.19	0.00	63.00	100.00	0.86

Table 1. Values of soil CO_2 efflux (in g m^{-2} d^{-1}) and $\delta^{13}C_{CO2}$ (in ‰ vs. VPDB) measured at sites ZAF06, ZAF08 and P78 during the studied period. Also shown are the corresponding meteorological data measured at the station located at Riposto. n.d. = not determined.

water temperature constantly a little higher than the average temperature of Mt. Etna ground water and the highest among the ground waters of the east flank of the volcano [Bonfanti et al. 1996, Brusca et al. 2001,

Date	P78		T_{air} °C	Rain mm	RH min %	RH max %	Wind m/s
	CO_2 flux	$\delta^{13}C_{CO2}$					
05/13/09	568	2.79	18.59	0.00	13.00	91.00	0.48
06/01/09	31608	2.53	22.09	0.00	15.00	87.00	1.77
06/15/09	11384	n.d.	23.15	0.00	12.00	77.00	1.08
06/26/09	24468	2.50	22.58	0.00	12.00	86.00	1.07
07/13/09	22838	2.30	24.57	0.00	12.00	90.00	1.04
07/30/09	15143	2.33	26.73	0.00	18.00	82.00	1.49
08/10/09	10446	n.d.	26.78	0.00	26.00	82.00	1.49
08/25/09	7213	2.16	26.97	0.00	19.00	94.00	1.26
09/07/09	5288	2.13	24.38	0.00	26.00	94.00	1.24
11/16/09	1378	2.47	15.53	0.00	22.00	98.00	0.50
12/10/09	3076	2.44	13.36	0.00	38.00	80.00	1.90
12/30/09	3054	2.58	15.77	0.00	25.00	95.00	0.63
01/07/10	1777	2.94	12.81	0.00	43.00	96.00	1.64
01/29/10	1160	2.65	9.57	0.00	53.00	90.00	0.69
02/12/10	307	2.90	7.05	1.00	42.00	97.00	0.84
03/01/10	904	3.10	14.88	0.00	41.00	97.00	1.00
03/19/10	733	2.87	10.46	0.00	30.00	97.00	0.88
04/09/10	5124	2.92	13.87	0.00	40.00	93.00	1.72
04/26/10	5027	2.68	16.19	3.00	27.00	97.00	1.04
06/08/10	2374	2.99	22.44	0.00	26.00	91.00	1.83
06/23/10	3297	1.60	22.65	0.00	25.00	66.00	1.46
07/14/10	4227	2.79	27.23	0.00	18.00	79.00	1.80
07/29/10	10535	2.64	24.88	0.00	23.00	93.00	1.23
08/26/10	7871	2.65	27.30	0.00	20.00	87.00	1.74
09/09/10	4362	2.66	24.50	5.60	47.00	94.00	1.64
09/23/10	3699	2.47	19.85	1.20	52.00	95.00	1.38
10/06/10	5419	2.55	21.49	0.00	47.00	94.00	0.50
10/22/10	3044	2.31	16.12	1.40	61.00	93.00	0.95
11/19/10	1991	2.29	13.44	0.00	39.00	99.00	0.40
12/07/10	2339	2.31	13.59	0.00	42.00	99.00	0.45

Table 2. Values of soil CO_2 efflux (in g m^{-2} d^{-1}) and $\delta^{13}C_{CO2}$ (in per ml vs. VPDB) measured at site P39 during the studied period. Also shown are the corresponding meteorological data measured at the station located at Paternò. n.d. = not determined.

Aiuppa et al. 2004].

A general positive correlation exists between the $\delta^{13}C_{CO2}$ values measured at sites P78, ZAF06 and ZAF08 and the corresponding values of soil CO_2 efflux (on a log_{10} scale) (Figure 2). In detail, assuming a log_{10} fit of data on the plots, the correlation coefficients (R^2) between the pairs of parameters for each site were calculated as +0.40 for site P78, +0.07 for site ZAF06 and +0.66 for site ZAF08. These results also confirm preliminary results based on previous measurements performed in the same area. A similar positive correlation was found at site P78 by Giammanco et al. [1998] and by Pecoraino and Giammanco [2005]. According to these authors, when CO_2 effluxes from site P78 were the highest, the corresponding values of $\delta^{13}C_{CO2}$ became very similar to the pristine magmatic ones assumed for Mt. Etna. More negative values of $\delta^{13}C_{CO2}$ would then indicate a higher degree of mixing between the magmatic component and the biogenic source in the soil gas, particularly evident at low CO_2 efflux values. This indicates that when CO_2 efflux becomes higher, magmatic CO_2 can reach the surface more efficiently, thus surmount-

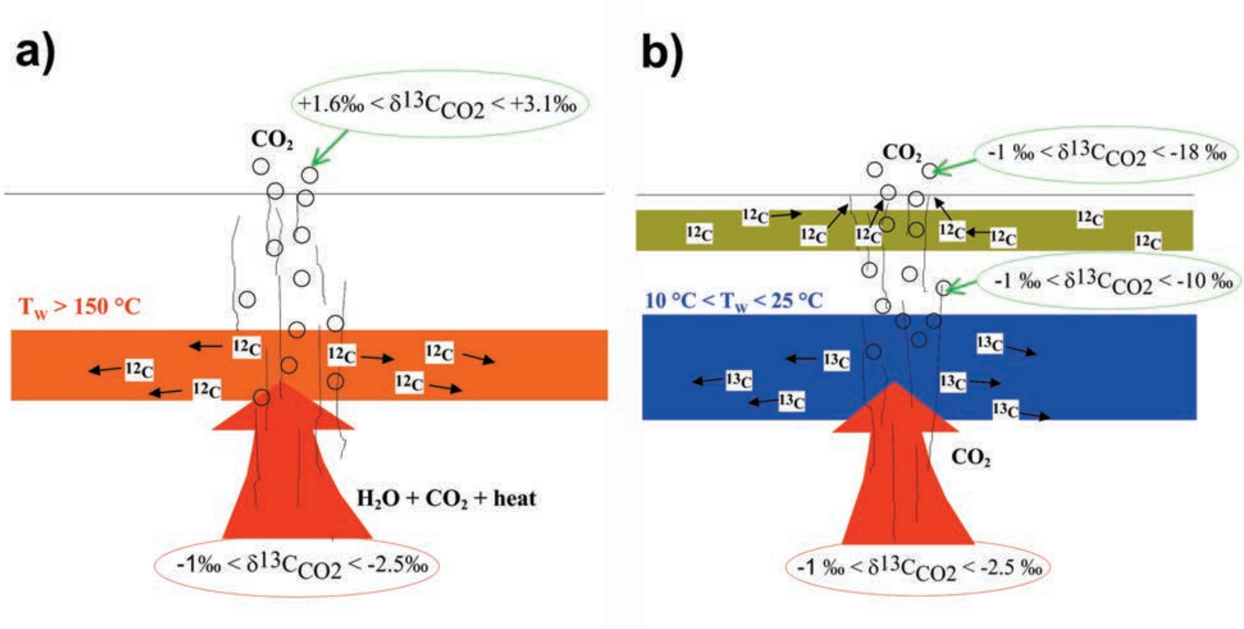

Figure 3. Schematic graphic models of the geochemical interactions between magmatic CO_2 gas and shallow fluids in the monitored sites: a) interaction between magmatic CO_2 and hydrothermal fluids (depicted as an orange horizontal layer) at site P39, with consequent positive shift of $\delta^{13}C$ values due to partition of ^{12}C into the liquid phase as HCO_3^-; b) interaction between magmatic CO_2 and cold ground water (depicted as a blue horizontal layer) at sites ZAF06, ZAF08 and P78, causing partition of ^{13}C into the liquid phase, followed by mixing with shallow biogenic CO_2 produced in the soil (depicted as a green horizontal layer) and consequent enrichment in ^{12}C in the gas phase.

ing the shallow biogenic component of the gas. This in turn confirms the transport of free gas (mostly CO_2) along preferential pathways in the crust that correspond to tectonic faults, where the local permeability is much higher than in the surrounding volcanic rocks (values of permeability in Etna rocks are in the range from 2.5×10^{-11} to 2.9×10^{-10} m^2, according to Aureli 1973 and Ferrara 1975) and where local ground water quickly becomes saturated with CO_2.

This behavior appears to be valid, more or less, for all three sites of the east flank of Mt. Etna investigated during this study. Interestingly, our findings are also in agreement with those of similar studies carried out at the Solfatara crater (Phlaegrean Fields, Italy) by Chiodini et al. [2008], who found a similar positive correlation between CO_2 efflux and the $\delta^{13}C_{CO2}$ values of the corresponding soil CO_2 efflux (i.e., C isotopes were not measured in soil gas samples, but at the outlet of the CO_2 efflux measurement device) from fumaroles located inside the crater and from diffuse emissions occurring both inside and outside of the crater. They explained the correlation as being due to a combination of three distinct statistical populations of samples: i) a high-flux population with a mean $\delta^{13}C$ value of -2.3±0.9‰, representative of pure hydrothermal degassing of CO_2 (this value was actually very similar to that of local fumarolic CO_2, that is -1.48‰); ii) a low flux population with a mean $\delta^{13}C$ value of about -19.4±2.1‰, representative of biogenic degassing of CO_2 (from microbial decomposition of organic matter in the soil, from plant residues or from root respiration); iii) an intermediate efflux population with a mean $\delta^{13}C$ value of about -9.8±3.7‰, representative of a mixture of the two above.

4.2. Temporal changes of the monitored parameters

The temporal patterns of the soil CO_2 efflux values for each site monitored, plotted on a $\log_{10}$ scale (Figure 4), show some common features between sites. A marked and sharp decrease was observed in mid-February 2009 simultaneously at sites P78, ZAF06 and ZAF08, to then give way to a steady increase since the end of March 2009. Further decreases were recorded, in

	P39	Tair	Rain	RH min	RH max	Wind
P39	1.00	0.51	-0.13	-0.55	-0.31	0.27
T° air		1.00	0.02	-0.56	-0.48	0.45
Rain			1.00	0.34	0.21	0.11
RH min				1.00	0.41	-0.15
RH max					1.00	-0.49
Wind						1.00

Table 3. Correlation matrix between the soil CO_2 efflux values measured at site P39 and the corresponding meteorological parameters measured at the station of Paternò.

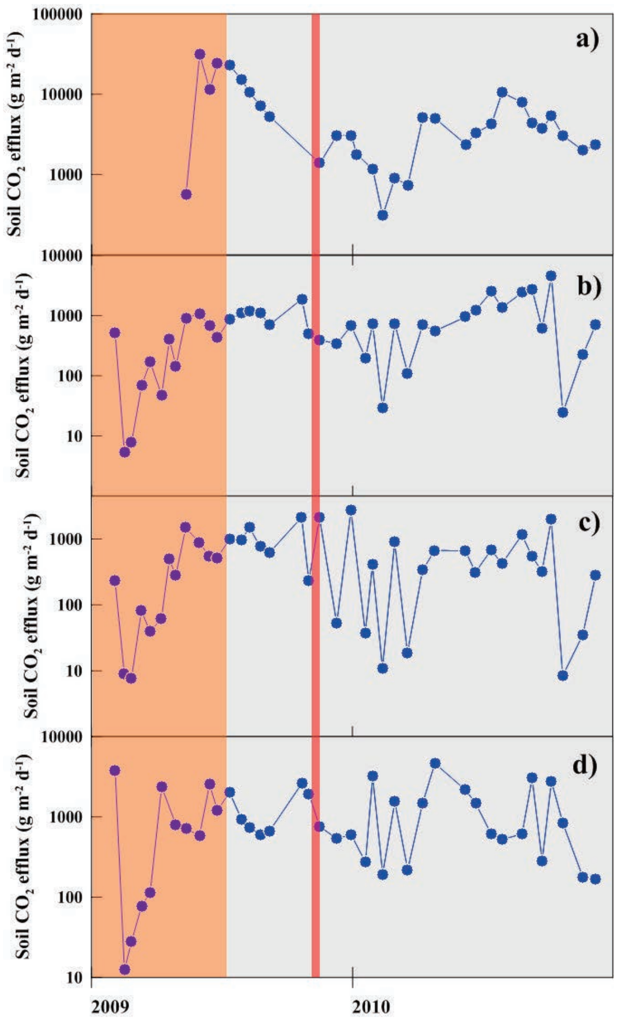

Figure 4. Temporal pattern of the soil CO_2 effluxes measured in the monitored sites during the study period: a) P39; b) P78; c) ZAF08; d) ZAF06. The pink area indicates the period of the 2008-2009 flank eruption. The vertical red line indicates the moment of the opening of the NSEC.

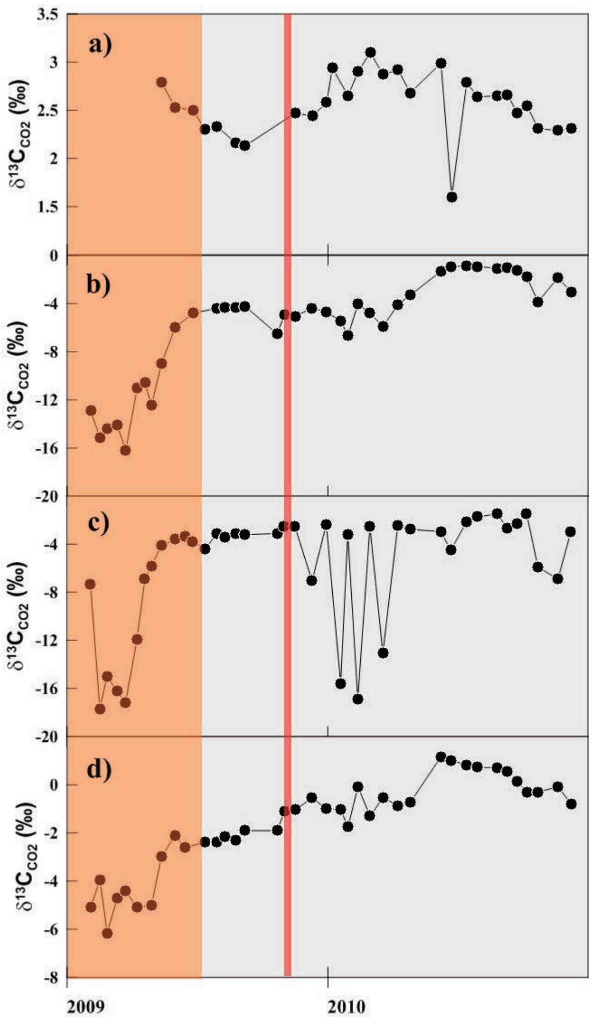

Figure 5. Temporal pattern of the $\delta^{13}C_{CO2}$ values measured in the monitored sites during the studied period: a) P39; b) P78; c) ZAF08; d) ZAF06. The pink area indicates the period of the 2008-2009 flank eruption. The vertical red line indicates the moment of the opening of the NSEC.

a more scattered way, from November 2009 to March 2010 and finally, following a sudden drop, in late October-December 2010, the latter observed only at sites ZAF08 and P78. The highest effluxes were observed during June-July 2009 at most of the sites, more evidently at P39. High effluxes were also recorded in April 2010 at site ZAF06, in July 2010 at P39 and, during September-October 2010, at more or less all sites. Site ZAF06 showed slightly more stable CO_2 effluxes after the above-mentioned period of very low values from January to March 2009. In order to determine whether the above changes were at least in part caused by variations in the main meteorological parameters, we performed a linear cross-correlation analysis of all the data, divided into areas (SE flank and E flank). The resulting correlation matrixes (Tables 3 and 4 for the area near Paternò and for that near Riposto, respectively), show no significant correlation between the considered parameters. All correlation coefficients were in the range between -0.56 and +0.7 and, apart from a very weak direct correlation between CO_2 efflux and air temperature at site P78 (R = +0.61), all other coefficients between soil CO_2 efflux and meteorological parameters had values between -0.56 and +0.51. This clearly suggests a non-environmental, probably volcanic, cause for the observed temporal changes in soil CO_2 efflux values (and by reflection also in $\delta^{13}C_{CO2}$ values) at all monitored sites.

The temporal patterns of $\delta^{13}C_{CO2}$ values (Figure 5) show dissimilar behavior between site P39 and the other three sites. As noted above, the $\delta^{13}C_{CO2}$ values at site P39 in general varied within a much narrower range (only about 1‰) than at the other sites and showed no appreciable correlation with the CO_2 efflux values. This points to a marked geochemical stability of the hydrothermal system beneath site P39, likely due to its large volume that makes it less sensitive, at least in terms of isotopic composition of the escaping CO_2, to changes in the input of high-enthalpy mag-

	ZAF06	ZAF08	P78	T_{air}	Rain	RH min	RH max	Wind
ZAF06	1.00	0.18	0.32	0.16	0.26	0.29	0.19	-0.31
ZAF08		1.00	0.51	0.45	0.00	0.18	0.07	-0.34
P78			1.00	0.61	0.33	0.35	0.31	-0.28
T° air				1.00	0.18	0.14	0.18	-0.35
Rain					1.00	0.11	0.17	0.02
RH min						1.00	0.56	-0.49
RH max							1.00	-0.24
Wind								1.00

Table 4. Correlation matrix between the soil CO_2 efflux values measured at sites ZAF06, ZAF08 and P78 and the corresponding meteorological parameters measured at the station of Riposto.

matic fluids coming from depth.

The other sites show, instead, a consistent behavior, marked by a more or less sharp positive shift of $\delta^{13}C$ values in April-May 2009, followed by a slower trend towards even more positive values. Carbon isotope values remained quite stable or decreased slightly from June to October 2010 to show a fairly more marked shift towards negative values in October-November 2010.

The overall picture arising from the above data indicates the significant arrival of deep magmatic CO_2 just before the end of the 2008-2009 flank eruption, reasonably related to emplacement of new gas-rich magma within relatively deep portions of the volcano and along conduits that were not directly connected with those feeding the ongoing flank eruption. This interpretation is strongly supported by other geochemical and geophysical parameters that were measured during the same period by the monitoring network of the Istituto Nazionale di Geofisica e Vulcanologia [Mattia et al. 2015]. In particular, the behavior observed in the temporal pattern of soil CO_2 efflux in early 2009 can be interpreted according to geochemical studies made both on soil CO_2 emissions from Mt. Etna [Giammanco et al. 1995, Bruno et al. 2001], and on crater fumarole emissions at Vulcano Island [Nuccio and Valenza 1992, 1998]. Strong decreases in the CO_2 output from soils or from fumaroles accompany early stages of magma motion towards the surface. In those cases, magma undergoes sudden pressure decreases, which causes marked exsolution of a separate vapor phase in the volatile-saturated melt and consequent partition of volatiles into the newly formed bubbles according to the different gas solubilities. Because of its low solubility in magma, CO_2 will be highly enriched in the separate vapor phase. The consequent decrease in the concentration of residual dissolved CO_2 in the uppermost portion of a magma body produces a kinetic diffusion effect that translates into an inward and upward migration of dissolved gas. This process results in an initial decrease of volatile fluxes released from the deep magma towards the surface. Subsequently, when CO_2-rich gas bubbles are able to escape from magma, outward advective fluxes of magmatic volatiles through the main pathways across the structure of the volcano (i.e., volcanic conduits, degassing faults) will markedly increase. The sequence observed in our data in early 2009, therefore, would represent a complete cycle of fresh magma transfer from deeper to shallower levels in the volcano. The simultaneous change in C isotope values would simply reflect the isotopic shift related with the above mentioned changes in the degree of mixing between the magmatic component and the biogenic source as function of CO_2 efflux.

After the end of the 2008-2009 eruption a further slow increase in magmatic CO_2 degassing was in general observed, suggesting that deep-coming magma moved further upward and accumulated into shallower portions of the volcanic system, thus releasing higher amounts of fluids. This in turn produced a higher input of high-enthalpy fluids into the shallow aquifers of Mt. Etna, thus raising the temperature of water in the subsurface hydrothermal systems within the volcano. This process would explain the further isotopic shift towards positive $\delta^{13}C$ values observed during the summer of 2010. Besides, the progressive pressurization of the shallow volcanic system as consequence of magma accumulation also reasonably led to the opening of the NSEC in early November 2009 and prepared for its following eruptive activity.

The sharp decrease in CO_2 efflux, combined with the slight negative shift of $\delta^{13}C$ values, observed since October 2010 at sites P78, ZAF08 and, to a lesser extent, also at ZAF06, might be the consequence of a sudden upward migration of magma. Marked transient decreases in soil CO_2 emissions at Mt. Etna were interpreted by Giammanco et al. [1995] as an indication of rapid upward migration of the gas source (i.e., a CO_2-oversaturated magma). Shallow magma up-rise produces a greater gas pressure gradient between the source of gas and the summit of the volcano, which greatly overcomes the gradient existing between the gas source and the peripheral areas. This large contrast favors the release of magmatic gas along the direction source-summit of the volcano, thus significantly dampening diffuse flank degassing. This hypothesis is also strongly supported by the following occurrence both of Strombolian activity at NSEC in late December 2010 and, mostly, of the long sequence of eruptive episodes since January 12, 2011; the latter episodes would testify the final arrival of magma at the surface.

5. Concluding remarks

The results of this study will help to better understand and define the physico-chemical mechanisms that rule the interactions occurring between deep CO_2 deriving from magma degassing inside Mt. Etna feeder conduit and the shallow fluids within the volcano. The observed temporal variations of the studied parameters are explained in terms of variable degree of geochemical interaction between high-enthalpy magmatic fluids and shallow ground water, as a function of the supply of magmatic gas from depth.

At high soil CO_2 effluxes, $\delta^{13}C_{CO2}$ values in the peripheral sites are similar to those found in the fumarole gases emitted close to the active summit craters of Mt. Etna. When this occurs, we can reasonably hypothesize that new gas-rich magma is accumulating in relatively deep (5-10 km) volumes within the volcano, causing a strong pressure increase in the whole volcanic system. Conversely, when flank CO_2 emission is low, values of $\delta^{13}C_{CO2}$ become more negative, pointing to a greater interaction with shallow non-magmatic fluids, in our case cold ground water and biogenic CO_2 [Giammanco et al. 1998, Pecoraino and Giammanco 2005].

Our results are encouraging for future monitoring of the eruptive activity of Mt. Etna. The sampling sites chosen are always easy to access under most weather conditions. Further, the sampling procedure is simple and the analytical methods are precise and reliable. A higher sampling frequency will certainly improve the temporal resolution on the studied parameters, thus permitting their use also as short-term indicators of the dynamics of Mt. Etna.

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*Corresponding author: Salvatore Giammanco,
Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo, Catania, Italy; email: salvatore.giammanco@ingv.it.