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# The buried caldera boundary of the Vesuvius 1631 eruption revealed by present-day soil CO<sub>2</sub> concentration

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#### ABSTRACT

Volcanic risk at Vesuvius is one of the highest in the world due to the ~670,000 inhabitants living in the Red Zone, the area exposed to both pyroclastic flows and tephra fallout, to be evacuated before renewal of any eruptive ac-tivity. The national emergency plan for Vesuvius builds its risk zonation on a scenario similar to the last sub-Plinian eruption, which occurred in 1631. This study aims at providing new insights on the geometry of the cal-dera associated with this historical eruption. The impact of past Vesuvius eruptions on present-day soil CO2 con-centration has been investigated by means of an extended geochemical survey carried out for identifying the circulation pathways of hydrothermal fluids inside the volcano. We performed 4018 soil CO<sub>2</sub> concentration mea-surements over the whole Somma-Vesuvius volcanic complex, covering an area of 50 km<sup>2</sup>. Besides relatively low values, the results show a significant spatial CO<sub>2</sub> concentration heterogeneity over Somma-Vesuvius ranging from the atmospheric value (~400 ppm) up to ~24,140 ppm. The summit of Vesuvius shows an area with anom-alous CO<sub>2</sub> concentrations well matching the crater rim of the 1906 eruption. Along the cone flanks, secondary CO<sub>2</sub> anomalies highlight a roughly circular preferential pathway detected along 8 radial profiles at distances between ~840 m and ~1150 m from the bottom of the present-day crater resulting from the last eruption in 1944. In depth review of the available literature highlights an agreement between this circle-like shaped anomaly and the 1631 sub-Plinian eruption caldera boundary. Indeed, based on the historical chronicles the depression produced by the 1631 eruption had a diameter of 1686 m, whereas the CO<sub>2</sub> circular anomaly indicates a diameter of 1956 m. Fi-nally, the results were compared with a 3-D density model obtained from a recent gravity survey that corrobo-rates both the literature and the CO<sub>2</sub> data in terms of potential buried structure at the base of the Vesuvius cone.

#### 1. Introduction

Carbon dioxide  $(CO_2)$  is the second most abundant volatile dissolved in magma after water, and starts exsolving at several kilometres depth due to its low solubility in silicate melts (Gerlach, 1986).  $CO_2$  rises up to the surface through permeable zones, which may also drain other

fluids such as hot steam. In fact, spatial correlations between soil gas and thermal anomalies suggest the existence of permeable pathways (e.g. faults and fractures) through which heat and mass transfer towards the surface (Chiodini et al., 2001a; Cardellini et al., 2003; Finizola et al., 2003, 2006; Lewicki et al., 2003; Brothelande et al., 2014).

Previous studies on volcanoes showed that extended soil CO<sub>2</sub> gas surveys allow to defining the main diffuse degassing structures representing structural planes of higher permeability (Barberi and Carapezza, 1994; Chiodini et al., 2001a; Finizola et al., 2002; Cardellini

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et al., 2003; Lewicki et al., 2003; Granieri et al., 2006; Barde Cabusson et al., 2009; Carapezza et al., 2009; Schütze et al., 2012). In particular, Chiodini et al. (2001a) was the first to define "diffuse degassing struc ture" (DDS) and where a specific structural survey was performed to in vestigate the relations between diffuse degassing and the patterns of fractures and faults. Then, Cardellini et al. (2003), quantified the concept of DDS. A soil gas survey permits quantifying the total soil diffuse degassing and its evolution with time, as well as defining structures (e.g. caldera borders, fractures, faults; Etiope et al., 1999; Finizola et al., 2002). Diverse techniques such as the dynamic CO<sub>2</sub> concentration method (Camarda et al., 2006) and the soil diffuse degassing method (Farrar et al., 1995; Chiodini et al., 1998; Granieri et al., 2013) can be used in soil CO<sub>2</sub> gas survey. It is worth noting that the soil CO<sub>2</sub> concen tration method is not a direct measurement of soil CO2 degassing and is limited being affected also by soil permeability. One of the critical prob lems in dealing with this method is the identification of the anomaly sources; in particular those related to deep or organic surface origins. In several cases, this issue can be overcome due to the significant highest concentration (more than one order of magnitude) of the deep origin anomalies related to magma degassing with respect to the shallow organic contribution. Probabilistic approaches (Sinclair, 1974) are also used to define the threshold between the different populations of the CO<sub>2</sub> anomalies (e.g. Chiodini et al., 1998, 2001a). The application of the soil CO<sub>2</sub> concentration method has yielded good results on volca noes characterized by 1) a permanent mild explosive activity (Strom boli Finizola et al., 2002, 2003, 2006, 2009; Revil et al., 2004, 2011; and Yasur volcanoes Brothelande et al., 2016), or 2) an intense degassing activity and close conduit (La Fossa of Vulcano Revil et al., 2008; Barde Cabusson et al., 2009; and La Soufrière de la Guadeloupe Allard et al., 1998; Brothelande et al., 2014).

The identification of structural limits (i.e. permeable zones) and their subsequent monitoring play a fundamental role in the timely de tection of likely precursors of a volcanic eruption (e.g. increase of gas emission) and its related hazard assessment. In case of unrest, gas flow increase along permeable zones can be related to (i) the increase in permeability due to seismic activity and pressurization, (ii) deformation processes or (iii) the increase in magma degassing. Despite the the oretical causes behind diffuse degassing, its monitoring is of the highest importance to understand processes involved in gas emission on active volcanoes.

The recognition of zones characterized by high permeability requires a high spatial resolution (i.e. spacing measurement from meters to few tens of meters). Several studies have permitted to identify the main ac tive structural boundaries dragging magmatic and hydrothermal fluids towards the surface (Finizola et al., 2002, 2003; Lewicki et al., 2003; Granieri et al., 2006; Carapezza et al., 2009; Mauri et al., 2012).

As in other dormant volcanoes, Vesuvius, a high risk volcano in the densely inhabited Neapolitan area, is affected by diffuse degassing as shown by several studies (Aiuppa et al., 2004; Frondini et al., 2004; Granieri et al., 2013). These studies were based on surveys performed by means of diffuse degassing techniques; namely through the soil diffuse  $CO_2$  flux (accumulation chamber method, Frondini et al., 2004; Granieri et al., 2013) and the soil  $CO_2$  concentration (Aiuppa et al., 2004). The two studies based on the soil  $CO_2$  flux aimed at quantifying the total diffuse degassing of the Vesuvius cone through randomly but homogeneously distributed measurements over the whole area, and identifying the main DDS. The latter aim was also pursued by Aiuppa et al. (2004).

The present study aims at identifying the DDS of the Vesuvius cone through the use, for practical reasons, of the soil  $\rm CO_2$  concentration method, as in Aiuppa et al. (2004), but at higher resolution (shorter measurement spacing and higher density of measurements). This study reports the results from several extensive field campaigns carried out over the entire Somma Vesuvius volcanic complex. The relatively low degassing activity at Vesuvius and the presence of areas covered by dense forests could limit the identification of anomalies related to

structural limits (i.e. faults and fractures), as magma degassing and su perficial organic respiration might yield similar CO<sub>2</sub> contributions. For this reason, throughout the fieldworks we strategically opted for a short spacing (20 m) between measurements to reveal anomaly widths, and thereby, to distinguish signal caused by structural elements from those of superficial organic origin. Indeed, several works (e.g. Finizola et al., 2002; Brothelande et al., 2014) have evidenced structural elements (i.e. crater and caldera boundaries or faults) characterizing low width CO<sub>2</sub> concentration anomalies (40 200 m). Results from the CO<sub>2</sub> measurements are compared with the historical literature related to the 1631 sub Plinian eruption, and also with the results of recent gravity measurements performed over the whole edifice, for better under standing the origin and the present day role of the main structural boundaries acting as preferential pathways for fluids inside the Vesu vius cone.

#### 2. Geological and structural settings

The Somma Vesuvius volcanic complex (Fig. 1) is a stratovolcano made of a multistage caldera, Mt. Somma, and a nested younger vol cano, Vesuvius. Its volcanism (i.e. from ~373 ka BP) is related to the sub duction of the Adriatic Ionian lithosphere below the Tyrrhenian basin (Fig. 1a).

During its eruptive activity, Mt. Somma has been partially disman tled by caldera collapses related to four Plinian eruptions, which oc curred in 22,030  $\pm$  175 (Pomici di Base), 8890  $\pm$  90 (Mercato), and  $3945 \pm 10$  yr cal BP (Avellino), and the Pompei eruption in A.D. 79 (Bertagnini et al., 1998; Cioni et al., 1999; Andronico and Cioni, 2002; Santacroce and Sbrana, 2003; Santacroce et al., 2008). The Vesuvius cone has grown within this multistage caldera (hereinafter Mt. Somma caldera) and has produced its last eruption in 1944 (Santacroce et al., 2008). At Vesuvius, periods of close conduit rest were usually interrupted by sub Plinian eruptions. Two large explosive events disrupted the growth of the cone after A.D. 79: the Pollena (A.D. 472; Rosi and Santacroce, 1983; Mastrolorenzo et al., 2002; Rolandi et al., 2004; Sulpizio et al., 2005), and the 1631 sub Plinian eruptions (Arnò et al., 1987; Rosi et al., 1993). The last eruptive open conduit pe riod of Vesuvius, characterized by lava effusions and mixed effusive explosive episodes, began after the 1631 eruption and lasted more than three centuries (Cioni et al., 2008) ending with the 1944 eruption. In particular, the 1794, 1822, 1872, and 1906 eruptions were the most intense events (VEI 2 3). All of them started with lava effusions followed by rapid transitions towards magmatic explosions with lava fountains, sustained columns, and occasionally by phreatomagmatic ex plosions (Santacroce, 1987; Santacroce et al., 1993; Marianelli et al., 1999; Arrighi et al., 2001). Since 1944, Vesuvius is characterized by low energy seismicity beneath the cone (e.g. max M3.6 on October 1999 and below M3 since 2000). Since 1944, temperature of fumarolic emissions in the summit area has decreased from typical magmatic values (>500 °C until the beginning of 1960), down to typical shallow hydrothermal steady state temperature, with water boiling tempera ture at that altitude, ~95 °C since the period 1995 2000 (Chiodini et al., 2001b; Del Pezzo et al., 2013).

From a tectonic point of view, Somma Vesuvius is located at the in tersection of two main northwest southeast and northeast southwest oriented regional fault systems (Fig. 1b; Ippolito et al., 1973; Pescatore and Sgrosso, 1973; Acocella and Funiciello, 2006; Principe et al., 2010). These two directions have been retrieved also from statistical analysis of fault planes at the scale of the edifice (Bianco et al., 1998), and from the eruptive fissures affecting the volcano flanks (Tadini et al., 2017) and the dykes cutting the Somma caldera walls (Marinoni, 1995). They have also been highlighted by large scale seis mic and gravity data, locating Somma Vesuvius over a major northeast southwest structure (Acocella and Funiciello, 2006, and ref erences therein). Additionally, some vents along the Mt. Somma flanks

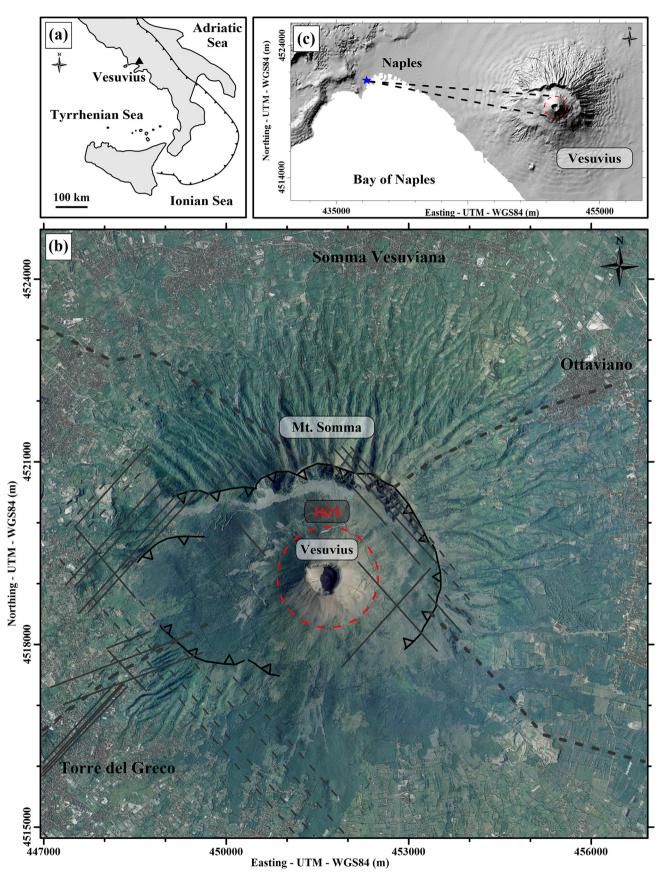


Fig. 1. a) Location of the Somma-Vesuvius volcanic complex (Italy) in the subduction context. b) DEM of the Somma-Vesuvius volcanic complex (Vilardo et al., 2008) with the Mt. Somma caldera boundary (Cioni et al., 1999). The regional faults (thick dashed lines), the main faults (dashed lines) and the fractures (solid lines) are from Principe et al. (2010). The red circle refers to the 1631 caldera limit measured by Carafa (1632). c) Map of the bay of Naples with the location of "Palazzo Reale" (blue star), from which Carafa (1632) painted and described the Vesuvius 1631 eruption (Fig. 2a). The black dashed lines highlight the relative view of the Vesuvius descriptions. The red dashed circle as in inset b.

tend to align along this fault system (Ventura and Vilardo, 2006; Tadini et al., 2017).

The present day Mt. Somma caldera boundary shows a substantial difference between its northern and southern sectors (Fig. 1b). In partic ular, the northern sector is less exposed to lava flows than the southern one. Indeed, the northern sector is almost fully covered by organic soil and vegetation, whereas the southern part is mostly covered by post A.D. 79 tephra deposits and lava flows (Ventura et al., 1999).

Present day Vesuvius crater rim (hereinafter 1944 crater rim; Fig. 1b) shows a sharp asymmetric topographic profile, which corre sponds to the intersection between lava fill of the crater left by the 1906 eruption and the crater produced by the 1944 eruption, whose edge lies southwest from the 1906 crater (Fig. 1b). This intersection is a preferential path for deep gas rising upwards and affecting the Vesu vius edifice (Frondini et al., 2004; Granieri et al., 2013). In addition, this intersection also separates the southwest crater area from the rest

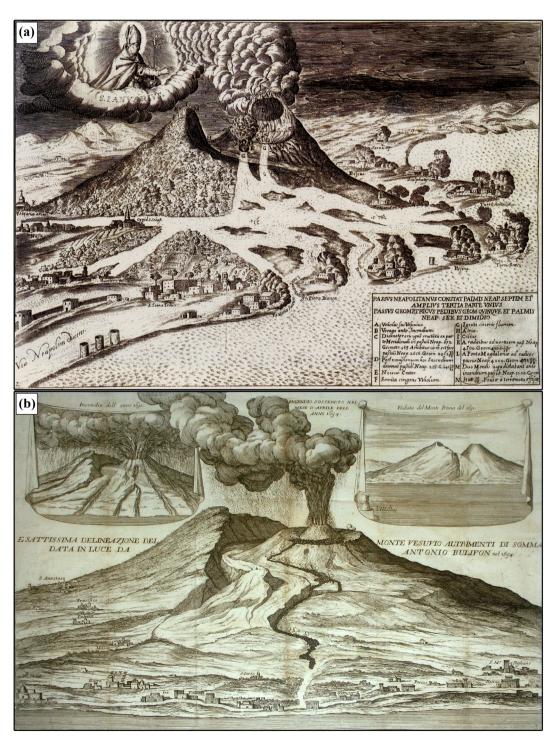


Fig. 2. a) Painting from "Palazzo Reale" (see Fig. 1c) of Somma-Vesuvius after the 1631 eruption (Carafa, 1632). The letters refer to Carafa's measurements for characterizing the 1631 caldera (legend in the lower right). b) Painting of Somma-Vesuvius showing the 1694 eruption (Bulifon, 1694) and the 1631 caldera partially filled at the time of the painting highlighting the impact of the 1631 eruption on the Vesuvius cone. The two insets represent the Vesuvius morphology prior (right) and during (left) the 1631 eruption.

of the crater highlighting an elevation discrepancy (i.e. ~120 m) in fa vour of the northeast sector of Vesuvius, which features the summit at 1281 m above sea level (a.s.l.).

#### 2.1. The 1631 sub Plinian eruption

In 1631, a sub Plinian eruption affected the structural setting of Ve suvius inducing a caldera collapse (e.g. Braccini, 1631, 1632; Carafa, 1632; Masculo, 1633; Nazzaro, 1989). Carafa's report (1632) contains a detailed reconstruction of the event. In particular, the authors men tioned that before the 1631 eruption, the Vesuvius summit was ~55 m higher than Mt. Somma, with a crater of ~1500 m and ~480 m in circum ference and diameter, respectively. These dimensions increased respec tively to ~5230 m and ~1690 m after the eruption. The scheme of such observations is reported in the painting displayed in Fig. 2a, showing the outline of the Somma Vesuvius shape, while Fig. 2b reveals the im pact of the 1631 eruption on the Vesuvius morphology. It is worth not ing that the right and left insets in Fig. 2b are respectively paintings of the Somma Vesuvius prior and during the 1631 eruption. In addition to the above morphological aspects, the location where the observations were done can be inverted through the paintings (Fig. 2a and b), which is more likely to be the *Palazzo Reale* in the city of Naples (blue star in Fig. 1c).

According to the chronicle summary compiled by Rosi et al. (1993), the 1631 eruption was characterized by four phases. It began with an opening phase in the early morning of 16 December after a sequence of strong earthquakes. An eruptive fissure opened and extended from the top to the base of the cone along the western flank (also visible on the paintings in Fig. 2a and b).

In a short time, ash and bombs were reported to fall on the rim of Mt. Somma (Anonymous, 1631a, 1631b). Then, a plume with a spectacular pine like shape was generated at the base of the eruptive fissure (Masculo, 1633), which then spread out south eastwards as volcanic ash clouds (Capece, 1631; Anonymous, 1632; Bove, 1632; Masino di Calvello, 1632; Rocco, 1632) up to Greece and Turkey (Constantinople), where ash fallout was reported (Giuliani, 1632).

On 17 December 1631, the subsequent phase of activity was accom panied by seismic shocks and ash fallout in the Neapolitan area. First, a 5 min earthquake occurred, which accompanied the collapse of the cal dera. From Naples, the collapse was seen as a swallowing of the cone (Rosi et al., 1993). Besides these observations, Carafa (1632) and Masculo (1633) reported an almost instantaneous destruction of the cone accompanied by a ground deformation dropping the sea level down by 6 m with a corresponding sea retreat reaching 2000 m followed by a 5 m high tsunami. Such observations were painted by Scipione Compagno (Guidoboni, 2008). Pyroclastic flows started simul taneously with the caldera forming collapse (Rosi et al., 1993). How ever, the pyroclastic flows were reported by the eyewitnesses in such a confused manner that for centuries the flows were interpreted as lava flows. The unequivocal emission of pyroclastic flows was first doc umented by Carracedo et al. (1993) and Rosi et al. (1993). Finally, the eruption ended with a final stage of ash and water vapour emission prior ash fallout and lahars along the slopes of the volcano (Rosi et al., 1993). When emissions of pyroclastic flows stopped, the first observa tions reported an elevation drop of the new Vesuvius summit below the Mt. Somma top, with caldera dimension clearly greater than the cra ter before the onset of the eruption (Masino di Calvello, 1632).

Based on sight observations (Guidoboni, 2008), the comparison and integration of field based physical volcanology data and chronicles (Rosi et al., 1993) with paleomagnetism study on volcanic hazards (e.g. pyroclastic flows; Carracedo et al., 1993) suggest that the 1631 eruption has played a major role on the morphological evolution of the Vesuvius cone.

Being the last major eruption of Vesuvius, the 1631 sub Plinian eruption was considered in the first national emergency plan, edited by the Italian Civil Protection Department, as the "maximum expected

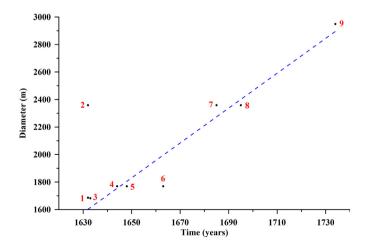
**Table 1**Diameter (*D*) and circumference (*C*) measurements of the 1631 caldera with the corresponding units and conversion in meters. *PN* stands for *Passi Napoletani* unit and *MI* for *Miglio Italiano* unit. \*Diameter calculated from direct circumference measurements. Numbers in brackets in the References column refer to Fig. 3.

Year	Diameter (D)			Circumference (C)			References
	Value	Unit	Value in m	Value	Unit	Value in m	
1632	872	PN	1686	2703	PN	5225	Carafa, 1632 <sup>(1)</sup>
1632	-	-	2359*	4	MI	7412	Braccini, 1631, 1632 <sup>(2)</sup>
1633	870	PN	1682	2730	PN	5277	Masculo, 1633 <sup>(3)</sup>
1644	-	PN	1769*	3	MI	5559	Evelyn, 1644 <sup>(4)</sup>
1648	-	-	1769*	3	MI	5559	Raymond, 1648 <sup>(5)</sup>
1663	-	PN	1769*	3	MI	5559	Magalotti, 1779 <sup>(6)</sup>
1685	-	PN	2359*	4	MI	7412	Burnet, 1699 <sup>(7)</sup>
1695	-	-	2359*	4	MI	7412	Drummond, 1845 <sup>(8)</sup>
1734	-	PN	2949*	5	MI	9265	Sorrentino, 1734 <sup>(9)</sup>

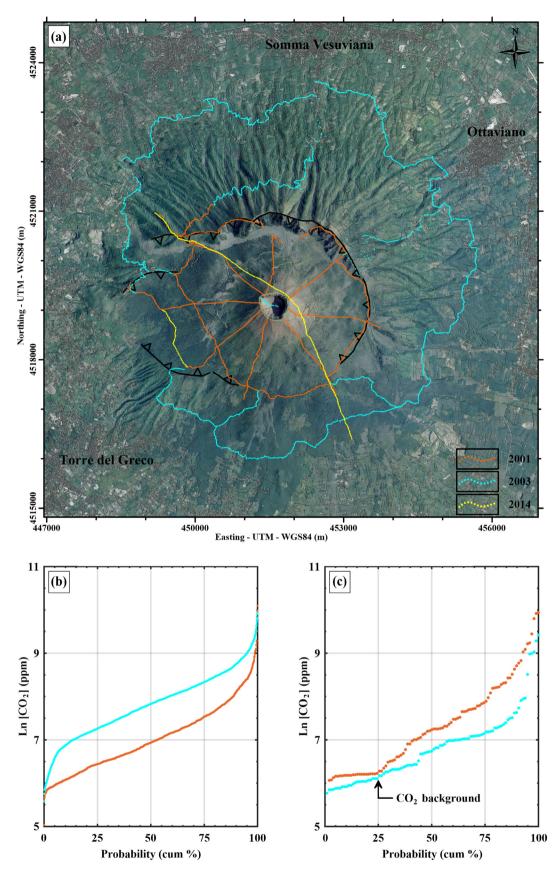
event" and reference scenario in case of renewal of the activity in the short or mid term (Barberi et al., 1995; DPC, 1995; Ricci et al., 2013). The current reference scenario for the updated plan (DPC, 2015) is still a sub Plinian event similar to that of 1631. The area immediately surrounding the volcano, named Red Zone, is prone to volcanic hazards related to flowage of pyroclastic density currents and lahars, and tephra fallout (Tadini et al., 2017). It includes 25 municipalities with ~670,000 inhabitants, which must be evacuated before the onset of the next erup tion (DPC, 2015).

#### 2.2. Observations from literature

In terms of morphological observations of the 1631 eruption, a crit ical review of the available literature highlights significant differences relative to the circumference (*C*) and diameter (*D*) of the crater pro duced by the eruption (e.g. Rosi et al., 1993). The two insets on Fig. 2b represent the Vesuvius morphology prior (right) and during (left) the 1631 eruption, while the main painting of Fig. 2b highlights the 1631 caldera partially filled at the time of the painting (1694 eruption; Bulifon, 1694). Table 1 summarizes the estimates of *D* from several au thors, which ranges from ~1682 to 2949 m. It is worth noting that the measurements were made by means of non universal measurement units (e.g. *Passo Napoletano PN* and *Miglio Italiano MI*), which require to be converted into meters (1.933 and 1853 m for the *PN* and *MI*, re spectively). Although most of the authors assessed *C* only (Table 1), Carafa (1632) and Masculo (1633) measured both *C* and *D*. It follows



**Fig. 3.** Measurements of the 1631 caldera diameter from literature. The blue dashed line represents the linear regression of diameter measurements, excluding the label 2 (see Section 2.1). Red numbers refer to the references presented in Table 1 (see numbers in brackets in the References column).



**Fig. 4.** (a) Location of the soil CO<sub>2</sub> concentration measurements performed on July 2001, July 2003 and March 2014 on the Somma-Vesuvius volcanic complex; (b) Probability plot technique (Sinclair, 1974) performed on the 2001 (orange) and 2003 (cyan) soil CO<sub>2</sub> concentration data acquired on the entire volcanic complex; (c) Probability plot technique (Sinclair, 1974) performed on the 2001 (orange) and 2003 (cyan) soil CO<sub>2</sub> concentration data acquired on the reiteration profile located on the crater rim (98 measurements; see Fig. 4a). The CO<sub>2</sub> background of the Somma-Vesuvius volcanic complex, obtained through the probability plot technique, is estimated around 550 ppm.

that for the cases where only *C* is provided, we estimated *D* by means of the relationship between *C* and *D*.

The available estimates of the 1631 caldera diameter are displayed in Fig. 3. With the exception of the measurement performed by Braccini (1632; label 2 in Fig. 3), diameter measurements indicate a nearly linear evolution with time of the caldera dimension, showing an increase of >1000 m in 100 years. This can be likely ascribed to the morpho structural evolution of the high angle and intensely fractured caldera wall (i.e. caldera wall collapses). Despite the difficulty in evaluating the data accuracy provided by the authors, those of Braccini have not been used for defining the regression line in Fig. 3, and were considered not re liable. Accordingly to the detailed description of the 1631 eruption features, also consistent with the reconstruction of Rosi et al. (1993), the data pro vided by Carafa (1632; label 1 in Fig. 3) have been taken as reference for performing a comparative analysis with the results of this investigation.

#### 3. Data acquisition and methodology

A total of 3949 measurements were carried out during two extensive one month field campaigns: 1) in July 2001 on the Vesuvius cone (1668 measurements, 20 m spacing; see Fig. 4a) and 2) in July 2003 in the low ermost part of the edifice including Mt. Somma area and also the profile going down into the actual Vesuvius crater (2281 measurements, 20 m spacing; see Fig. 4a). A common profile of 98 measurements was carried

out along the crater rim both in July 2001 and July 2003 (Fig. 4a). The two datasets were both acquired in July (summer season) to mitigate the effect of external parameters on soil CO<sub>2</sub> concentration, especially those induced by variation of soil moisture. Indeed, soil was relatively dry for all the measurements. In March 2014, a short profile (69 mea surements, 20 m spacing) was added to achieved covering the western lower flank of the Vesuvius cone increasing the total amount of mea surements up to 4018. Besides this dataset, during the 2014 campaign, we also acquired a northwest southeast oriented ~7 km long profile (349 measurements, 20 m spacing; Fig. 4a; Poret et al., 2016). Each mea surement was geo referenced by means of a hand held GPS. During the two main campaigns, data were collected following eight radial profiles extending from the 1944 crater rim (Fig. 4a) down to the base of the cone (~700 m a.s.l.). For achieving a measurement mesh representative of the entire volcanic complex, we closed the grid by adding three circu lar profiles 1) along the 1944 crater rim, 2) at the base of the Vesuvius cone, and 3) the largest and topographically lowermost one that in cludes the Mt. Somma (Fig. 4a).

Soil gas was collected by pumping with a 100 ml syringe through a 3 mm diameter tube inserted at 30 cm depth.  $CO_2$  concentration was measured by injecting the samples into two infrared spectrometers. The high variability of  $CO_2$  concentration, as expected for dormant vol canoes and surrounding areas, motivated the use of two spectrometers. One spectrometer was used to detect and measure low concentrations

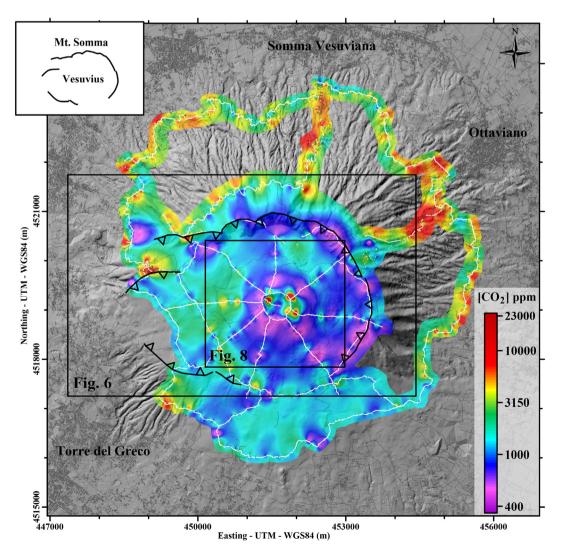


Fig. 5. Soil CO<sub>2</sub> concentration map of the Somma-Vesuvius volcanic complex. White dots show the CO<sub>2</sub> measurements. The reported Mt. Somma caldera limit (line with triangles) is extracted from Cioni et al. (1999). The rectangles localize the extension of Figs. 6 and 8.

(<3000 ppm), while the other is set for higher concentrations (i.e. 3000 100,000 ppm). The analytical uncertainty related to the  $CO_2$  concentration retrieval is estimated at  $\pm 5\%$  (Finizola et al., 2009).

Considering the uneven distribution of the data (2001 and 2003 cam paigns), we produced the  $CO_2$  concentration map by using the Kriging method following two steps, as suggested by Finizola et al. (2002). First, we interpolated through a regional mesh with a resolution of 10 times the sampling step (i.e.  $200 \times 200$  m). Then, the resulting interpolation was integrated into the data for locally interpolating at higher resolution ( $40 \times 40$  m). The largest areas with no data were blanked.

#### 4. Results and discussion

Before discussing the soil  $CO_2$  concentrations associated with the Somma Vesuvius volcanic complex, we tested the dataset through the probability plot technique (Sinclair, 1974; Chiodini et al., 1998, 2001a, 2017; Frondini et al., 2004), which can be used for displaying the data and highlighting the different  $CO_2$  populations. First, we considered all the data (2001 and 2003) and the probability plot technique displays values significantly higher in 2003 with respect to 2001 (Fig. 4b). This re sult is attributed to the locations of the 2003 measurements on the north ern flank of Mt. Somma, where dense forests cover investigated area. Then, we also tested the probability plot technique on the 98  $CO_2$  mea surements collected along the 1944 crater rim during both campaigns. The result displays a significant decrease in soil  $CO_2$  concentration be tween July 2001 and July 2003 (Fig. 4c). As the crater rim is not vegetated, the decrease can be attributed to a slight decrease in magma degassing.

#### 4.1. Soil CO<sub>2</sub> concentration on the Somma Vesuvius volcanic complex

The soil  $CO_2$  concentrations over the Somma Vesuvius complex shows relatively low values, ranging between ~400 and ~24,140 ppm (Fig. 5) compared to other active volcanoes. Indeed, La Fossa of Vulcano

(Barde Cabusson et al., 2009), La Soufrière de la Guadeloupe (Allard et al., 1998; Brothelande et al., 2014), and Furnas in the Azores (Viveiros et al., 2010) are characterized by CO<sub>2</sub> concentrations close to 1000,000 ppm (i.e. 100% in volume).

Fig. 5 highlights the areal distribution and the high heterogeneity of the soil CO<sub>2</sub> concentration for the entire Somma Vesuvius area, from which we can distinguish the following 3 main sectors: 1) the actual summit area of the Vesuvius cone, exhibiting the highest CO<sub>2</sub> concentra tion values (up to ~24,140 ppm) sometimes associated with sub fumarolic activity; 2) the flanks of the Vesuvius cone down to the Mt. Somma caldera, characterized by CO<sub>2</sub> background values below 1000 ppm with scattered CO<sub>2</sub> peaks; 3) the area located outside the Mt. Somma caldera (i.e. N, E, and W flanks), having CO<sub>2</sub> values in aver age higher (up to 15,000 ppm) than inside the structure. The transition between the last two sectors appears to coincide with the Mt. Somma caldera boundary. However, it is worth noting that this method does not permit distinguishing between CO<sub>2</sub> issued from deep degassing (i.e. volcanic origin) or produced by "soil respiration" (i.e. biogenic ori gin; Mielnick and Dugas, 2000; Aiuppa et al., 2004). Indeed, by compar ing Fig. 5 with Fig. 1b we observe that sector 3 is dominated by a dense forest being responsible of the abundant presence of CO<sub>2</sub>. As a conse quence, results obtained from the data collected on the northern slopes of Mt. Somma appear of little significance in the context of volcano related investigations (i.e. to position buried caldera margins and other structural elements such as faults and fractures). Although less in tensive in terms of soil CO<sub>2</sub> concentrations, this is also the case of the bottom of the inner part of the Mt. Somma caldera (i.e. sector 2). In con trast, sector 1 has almost no vegetation but shows localized CO<sub>2</sub> anom alies in the summit area, which are assumed to be related to deep degassing (i.e. volcanic origin; Aiuppa et al., 2004; Frondini et al., 2004).

Taking into consideration the soil CO<sub>2</sub> degassing over the entire vol canic edifice, weak, moderate, and strong degassing areas can be ob served, accordingly to other volcanoes (e.g. Galeras, Poas and Rincon

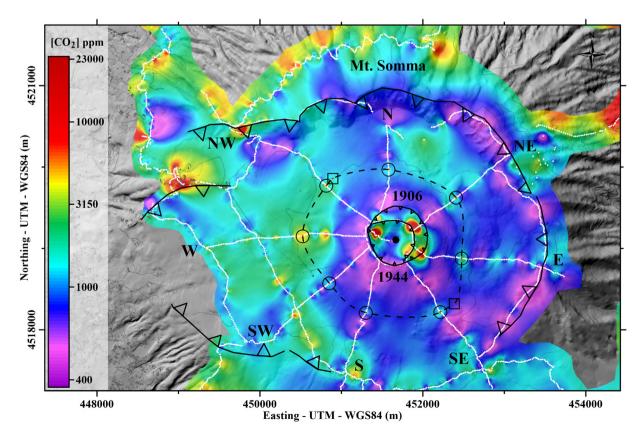


Fig. 6. Soil CO<sub>2</sub> concentration map. Circles refer to the CO<sub>2</sub> peaks identified along the 8 radial profiles while squares refer to the NW-SE profile (Poret et al., 2016; details in Table 2). Mt. Somma caldera rim is from Cioni et al., 1999. The 1906 and 1944 crater rims are from Andronico et al., 1995; Santacroce and Sbrana, 2003. Black dot shows the bottom of the 1944 crater.

de la Vieja Williams Jones et al., 2000; Misti Finizola et al., 2004; Stromboli Finizola et al., 2002). The weak degassing areas in the upper part of a volcano have been often associated with self sealing processes induced by hydrothermal activity inside the edifice (e.g. Vulcano, Barde Cabusson et al., 2009). This interpretation could also be sug gested for the Somma Vesuvius.

#### 4.2. Soil CO<sub>2</sub> concentration on the flanks of the Vesuvius cone

Fig. 6 shows that  $\rm CO_2$  anomalies located near the present day sum mit area of Vesuvius are well constrained within the 1906 crater bound ary, showing significant  $\rm CO_2$  degassing accompanied by low temperature fumarolic activity. This observation may be related to the location of the main conduit of the 1906 eruption that, during which a peculiar sustained gas jet phase occurred and was described in detail in Perret (1924), and then reported in Bertagnini et al. (1991) and Mastrolorenzo et al. (1993).

It is worth noting that the 8 radial profiles (i.e. N, NE, E, SE, S, SW, W, and NW) tend to have the same  $CO_2$  concentration trend with a peak at ~1 km from the bottom of the 1944 crater (in average 997 m, standard deviation:  $\sigma=103$  m). The nearly circular distribution of the  $CO_2$  peaks around the summit area together with the distribution and loca tion of the main volcano tectonic and regional geological structures (Bianco et al., 1998; Ventura et al., 1999; Principe et al., 2010) as well

as the distribution of the eccentric eruptive vents and fractures (Linde et al., 2017 and references therein), lead to assume these anomalies to be independent from the regional volcano tectonic structures men tioned in Section 2 (Fig. 1b).

Comparing the identified  $CO_2$  anomalous peaks (Fig. 6) with the pre vious studies (Frondini et al., 2004; Granieri et al., 2013), no similar anomalies have been highlighted. Indeed, the measurements of Granieri et al. (2013) are located at higher elevation on the cone than the detected  $CO_2$  anomalous peaks (see Fig. 1a therein), and measure ments of Frondini et al. (2004) only partially cover the Vesuvius edifice with higher measurement spacing (i.e. lower spatial resolution than this study; see Fig. 1c therein).

In particular, by analysing the 8 profiles from the 1944 crater rim to wards the base of the cone shows a systematic local  $CO_2$  increase (ar rows in Fig. 7a). The  $CO_2$  concentration peaks range between 1426 and 7410 ppm (Table 2). In addition, the same  $CO_2$  anomalies were ob served along the NW SE profile carried out in 2014 (squares in Fig. 6; Table 2; Ricci et al., in prep.), which crossed the entire edifice with a measurement spacing of 20 m (Poret et al., 2016).

Each of the ten radial profiles (i.e. circles and squares in Fig. 6), shows a single  $CO_2$  peak but the W profile, along which two peaks are identified (Figs. 6 and 7a). One peak is located along the western slope of the cone (i.e. 500 700 m from the crater rim), whereas the second is at the base of the cone (i.e. 800 1100 m from the crater rim).

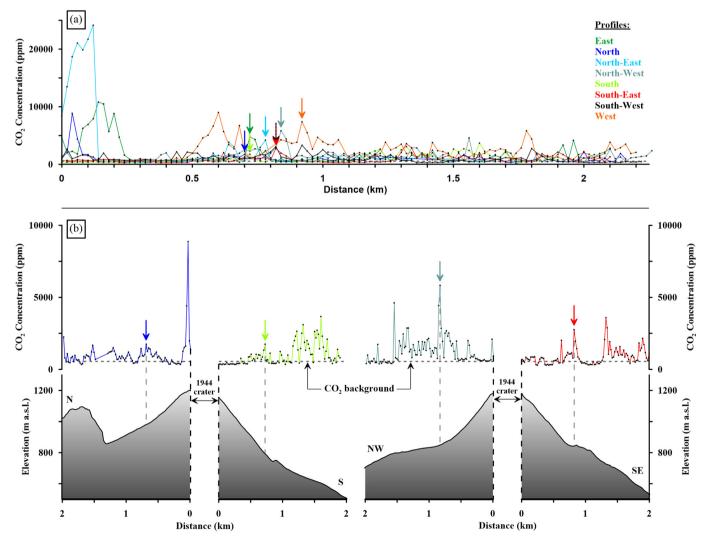


Fig. 7. a) Soil CO<sub>2</sub> concentration profiles measured on the Vesuvius cone. Distance is set from the top of the actual crater rim towards the base of the cone. The arrows refer to the CO<sub>2</sub> peaks described in Table 2. The CO<sub>2</sub> background for the Vesuvius cone, 550 ppm, was identified by means of the probability plot method (Sinclair, 1974). b) Example of the N-S and NW-SE CO<sub>2</sub> concentration profiles with the corresponding topography.

**Table 2** Location of the  $10\ CO_2$  concentration peaks identified on each radial profile with the corresponding  $CO_2$  concentration value, elevation, horizontal distance from the 1944 crater rim, and horizontal distance from the bottom of the 1944 crater.

Longitude UTM WGS 84	Latitude UTM WGS 84	[CO <sub>2</sub> ] (ppm)	Altitude (m a.s.l.)	Distance from the 1944 crater rim (m)	Distance from the bottom of 1944 crater (m)
451579	4519969	1749	975	675	869
452406	4519627	4224	933	751	903
452475	4518878	4776	950	694	838
452215	4518219	2766	840	873	1041
451300	4518212	1748	790	735	966
450851	4518573	1426	791	747	976
450524	4519150	7410	797	847	1146
450814	4519772	5826	845	790	1084
450894	4519861	2449	848	804	1082
452386	4518321	2024	844	827	1063
	UTM WGS 84 451579 452406 452475 452215 451300 450851 450524 450814 450894	UTM WGS 84  451579 4519969 452406 4518278 452475 4518219 451300 4518212 450851 4518573 450524 4519150 450814 4519772 450894 4519861	UTM WGS 84 (ppm) 84 UTM (ppm) 84 4519969 1749 452406 4519627 4224 452475 4518219 2766 451300 4518212 1748 450851 4518573 1426 450524 451950 7410 450814 4519772 5826 450894 4519861 2449	UTM WGS 84 (ppm) (m a.s.l.)  451579 451969 1749 975 452406 4519627 4224 933 452475 4518878 4776 950 452215 4518219 2766 840 451300 4518212 1748 790 450851 4518573 1426 791 450524 4519150 7410 797 450814 4519772 5826 845 450894 4519861 2449 848	UTM WGS         UTM WGS 84         (ppm)         (m a.s.l.) from the 1944 crater rim (m)           451579         4519969         1749         975         675           452406         4519627         4224         933         751           452475         4518878         4776         950         694           452215         4518219         2766         840         873           451300         4518212         1748         790         735           450851         4518573         1426         791         747           450854         4519772         5826         845         790           450894         4519861         2449         848         804

Considering the distance between the crater rim and these two peaks, the one at the base of the cone seems to be likely linked with those of the other profiles. Therefore, only this anomaly located at the base of the cone will be considered for the W profile in this study (Table 2).

The circular shape of the observed  $CO_2$  local maxima (Table 2) centred on the 1944 crater (dashed line in Fig. 6), is characterized by the short lateral extension (i.e. ~40 140 m length), and the same

order of magnitude for  $CO_2$  concentration (Table 2). Furthermore, the elevation of the  $CO_2$  peaks varies within <200 m (from ~790 to ~975 m a.s.l.). The horizontal distance from the 1944 crater rim varies between ~675 and ~873 m, whereas that from the bottom of the 1944 crater between ~838 and ~1146 m. The rather symmetric shape ob served through the  $CO_2$  anomalies indicates an average diameter of ~1956 m near the base of the Vesuvius cone.

The circular shape from the identified CO<sub>2</sub> peaks (hereinafter "CO<sub>2</sub> limit") suggests the presence of a buried structural feature (dashed line in Fig. 6). On the basis of the historical reports (Carafa, 1632; Rosi et al., 1993), the caldera rim of the 1631 sub Plinian eruption, with a ~1686 m diameter (Table 1), appears to be similar to the CO<sub>2</sub> limit. We quantitatively compared the CO<sub>2</sub> limit with the inferred 1631 cal dera boundary (Carafa, 1632), which are both displayed in Fig. 8. Con sidering the missing information related to the exact location and geometry of the vent in the 1631 eruption, the structural boundary has been centred on the 1944 crater bottom by assuming that the pres ent conduit of Vesuvius remained unchanged since the 1631 eruption, being consistent with Tadini et al. (2017). Furthermore, the location from which the 1631 caldera has been measured (Carafa, 1632; Fig. 1c) implies the assumption of a circular shape geometry. However, as observed on other volcanoes, caldera boundaries are roughly circular but can also present irregularities due to caldera collapse processes and pre existing structural setting (e.g. Orsi et al., 1999; Roche et al., 2000; Merle and Lénat, 2003; Acocella, 2007; Capuano et al., 2013). The CO<sub>2</sub> limit (Fig. 8) illustrates such an irregular shape, which could not be

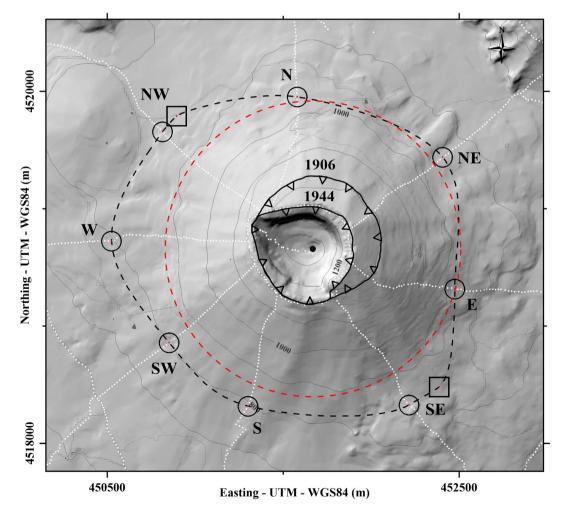


Fig. 8. Comparison between the 1631 caldera (Carafa, 1632) and the CO<sub>2</sub> limit. Circles refer to the CO<sub>2</sub> peaks identified along the 8 radial profiles, while squares refer to the NW-SE profile (Poret et al., 2016; see Table 2). Red dashed line is the 1631 caldera boundary (from Carafa, 1632, and Rosi et al., 1993) and the black dashed line is the limit inferred from the CO<sub>2</sub> concentration peaks. Black dot shows the bottom of 1944 crater.

observed by Carafa (1632) from his viewpoint (Fig. 1c). Considering a non perfectly circular boundary, the average diameter of the CO<sub>2</sub> limit deriving from the anomalous values is 1956 m ( $\sigma$  = 129 m), having the largest diameter (~2125 m) oriented north west south eastwards, and the shortest one (i.e. ~1834 m) along the north south profile.

The 1631 caldera boundaries from Carafa (1632) and the  $\rm CO_2$  limit suggested in this study (Fig. 8) coincide in shape, with differences along the radials ranging from 0 (i.e. perfect fit) to ~307 m (in average ~139 m wider than Carafa's measurements). It is worth noting that the comparison between Carafa's measurements and the results of this study for determining the 1631 caldera dimension is only qualita tive due to the large uncertainties in both methods. Indeed, by calculat ing remotely Carafa has assumed a perfect circular shape, observing partially the caldera rim (see Fig. 1c). Furthermore, it is also difficult to assess the degree of accuracy of the painting. Besides, soil  $\rm CO_2$ 

concentration survey suffers from uncertainties relative to the soil per meability that partially controls the soil  $CO_2$  concentration. Moreover, fracture orientations drive  $CO_2$  towards the surface with a certain angle. Nonetheless, the 1631 sub Plinian eruption is the last major event at Vesuvius, producing relatively young fractures, potentially having today a greater permeability than the surrounding environment. However, the caldera dimension discrepancies can also reflect the evolution of the caldera walls, with local enlargement of the rim related to landslides affecting the inner and dip caldera slopes.

In Fig. 6, the west flank of the Vesuvius cone shows two  $CO_2$  concentration anomalies, reflecting a more complex structure (see also Fig. 7a). To better constrain the effect of the 1631 caldera boundary on the present day structure of the Vesuvius cone, the  $CO_2$  results were also compared with those of a 3 D density model obtained from a recent gravity survey (Linde et al., 2017). Fig. 9 shows the overlapping of the

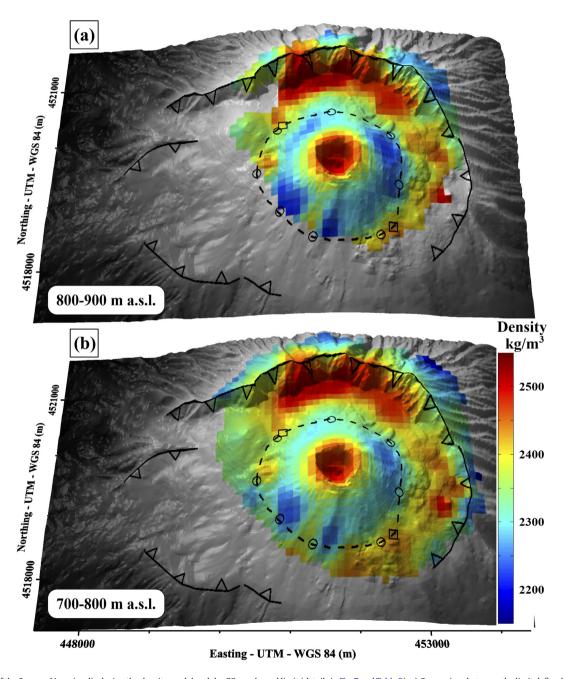


Fig. 9. 3-D view of the Somma-Vesuvius displaying the density model and the CO<sub>2</sub> peaks and limit (details in Fig. 7 and Table 2). a) Comparison between the limit defined by the CO<sub>2</sub> peaks with a horizontal density slice between 800 and 900 m a.s.l.; b) The same comparison but for a horizontal density slice between 700 and 800 m a.s.l. Circles refer to the CO<sub>2</sub> peaks identified along the 8 radial profiles, while squares refer to the NW-SE profile (Poret et al., 2016; see Table 2). Mt. Somma caldera rim is from Cioni et al., 1999.

CO<sub>2</sub> limit with two horizontal density slices at 800 900 m and 700 800 m a.s.l. (respectively Figs. 9a and b). The two elevation inter vals are motivated by the CO<sub>2</sub> peak elevations (Table 2). Indeed, the av erage elevation of the CO<sub>2</sub> limit is 865 m a.s.l. The two elevation intervals were therefore chosen for embracing both the average eleva tion of the supposed 1631 caldera rim as well as its buried structure. The comparison between CO<sub>2</sub> and the density model highlights the link between the 1631 caldera and the density distribution inside the Vesuvius cone. In addition, Fig. 9 emphasizes a less dense sector (i.e. 2200 2300 kg/m<sup>3</sup>) inside the 1631 caldera boundary defined by the CO<sub>2</sub> limit, suggesting that the 1631 caldera was refilled by volcanic products that are less dense than the outer and older part of the Vesu vius cone. These gravimetric results clearly show that the 1631 erup tion induced a significant decrease in the global density of the products emitted before and after this major explosive event. Such a lower density distribution is commonly observed on many calderas (e.g. Froger et al., 1998; Brothelande et al., 2016), and strongly supports the hypothesis that the identified CO<sub>2</sub> limit defines the 1631 caldera boundary.

#### 5. Conclusions

We have carried out 4018 soil CO<sub>2</sub> measurements along profiles cov ering the whole Somma Vesuvius volcanic complex (50 km<sup>2</sup>) with a measurement spacing of 20 m. The results allowed sub dividing the studied area in three sectors: 1) the present day summit area of the Ve suvius cone with the highest CO<sub>2</sub> concentration value (~24,140 ppm) lo cated inside the partially buried 1906 crater rim, 2) the flanks of the Vesuvius cone characterized by weak CO<sub>2</sub> concentrations, and 3) the area located outside Mt. Somma caldera with moderate CO<sub>2</sub> concentra tions. This study focuses on the short spatial extension anomalies mea sured on the flanks of the Vesuvius cone. The CO<sub>2</sub> data revealed a roughly circular degassing structure located between 790 and 975 m a.s.l. This CO<sub>2</sub> limit was compared with a review of the historical litera ture available showing similar dimensions of the 1631 caldera boundary (i.e. diameter of ~1686 m). The quantitative analysis indicates radial dis crepancies up to 307 m. The impact of the 1631 caldera on the inner structure of the Vesuvius cone has been also identified by comparing the resulting CO<sub>2</sub> limit with a recent 3 D density model obtained from gravity measurements. This model clearly shows lower density values inside the Vesuvius cone, which suggests a post 1631 filling by volcanic products. This study highlights the importance of carrying out soil CO<sub>2</sub> measurements using a short spacing for identifying weak and local anomalies potentially defining the inner structure of a volcanic edifice. Indeed, by means of 20 m measurement step, this study identified and localized the present day weak boundary produced by the 1631 caldera. This information is pivotal for monitoring and assessing the volcanic hazards, permitting to identify the potential areas prone to the opening of new eruptive vents.

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