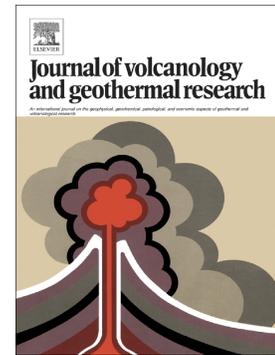


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The buried caldera boundary of the Vesuvius 1631 eruption revealed by present-day soil CO₂ concentration

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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 activity. 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 caldera associated with this historical eruption. The impact of past Vesuvius eruptions on present-day soil CO₂ concentration 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 4,018 soil CO₂ concentration measurements over the whole Somma-Vesuvius volcanic complex, covering an area of 50 km². Besides relatively low values, the results show a significant spatial CO₂ 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 anomalous CO₂ concentrations well matching the crater rim of the 1906 eruption. Along the cone flanks, secondary CO₂ anomalies highlight a roughly circular preferential pathway detected along 8 radial profiles at distances between ~840 m and ~1,150 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 1,686 m, whereas the CO₂ circular anomaly indicates a diameter of 1,956 m. Finally, the results were compared with a 3-D density model obtained from a recent gravity survey that corroborates both the literature and the CO₂ data in terms of potential buried structure at the base of the Vesuvius cone.

Keywords: Somma-Vesuvius, soil CO₂ concentration, 1631 sub-Plinian eruption, carbon dioxide, caldera.

1. Introduction

Carbon dioxide (CO₂) 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). CO₂ 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 CO₂ 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 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 structure” (DDS) and where a specific structural survey was performed to investigate 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 CO₂ 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 CO₂ gas survey. It is worth noting that the soil CO₂ concentration method is not a direct measurement of soil CO₂ degassing and is limited being affected also by soil permeability. One of the critical problems 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 CO₂ anomalies (e.g. Chiodini et al., 1998; 2001a). The application of the soil CO₂ concentration method has yielded good results on volcanoes characterised by 1) a permanent mild explosive activity (Stromboli – 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 detection 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 theoretical 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 active 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 CO₂ flux (accumulation chamber method, Frondini et al., 2004; Granieri et al., 2013) and the soil CO₂ concentration (Aiuppa et al., 2004). The two studies based on the soil CO₂ 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 CO₂ 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 superficial organic respiration might yield similar CO₂ 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 CO₂ concentration anomalies (40-200 m). Results from the CO₂ 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 understanding the origin and the present-day role of the main structural boundaries acting as preferential pathways for fluids inside the Vesuvius 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 volcano, Vesuvius. Its volcanism (i.e. from ~373 ka BP) is related to the subduction of the Adriatic-Ionian lithosphere below the Tyrrhenian basin (Fig. 1a).

During its eruptive activity, Mt. Somma has been partially dismantled by caldera collapses related to four Plinian eruptions, which occurred in $22,030 \pm 175$ (Pomici di Base), $8,890 \pm 90$ (Mercato), and $3,945 \pm 10$ 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 period of Vesuvius, characterised 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 explosions (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 (more than 500°C until the beginning of 1960), down to typical shallow hydrothermal steady state temperature, with water boiling temperature at that altitude, $\sim 95^{\circ}\text{C}$ 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 intersection 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 seismic and gravity data, locating Somma-Vesuvius over a major northeast-southwest structure (Acocella and Funiciello, 2006, and references therein). Additionally, some vents along the Mt. Somma flanks tend to align along this fault system (Ventura and Vilardo, 2006; Tadini et al., 2017).

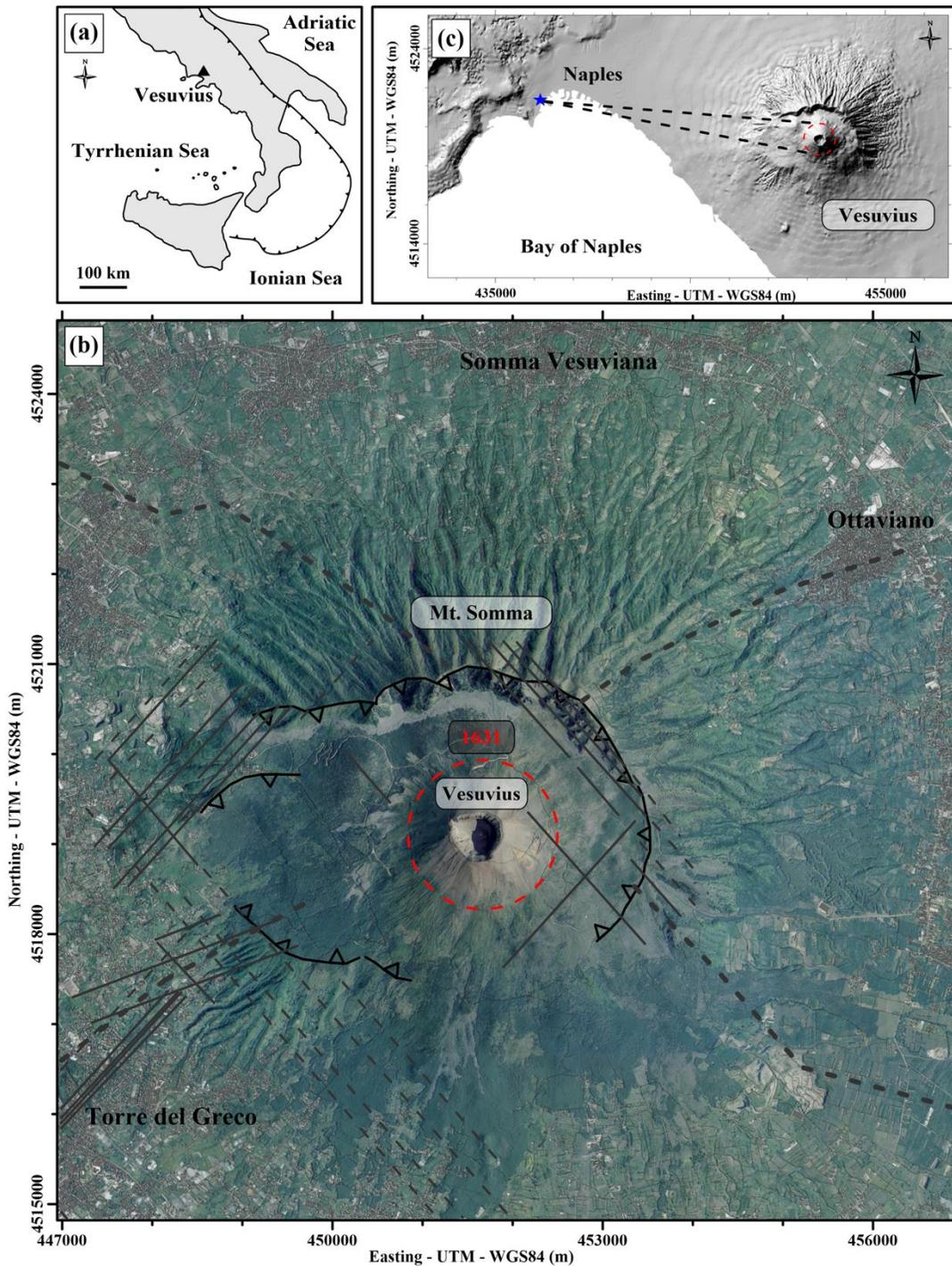


Figure 1: a) Location of the Somma-Vesuvius volcanic complex (Italy) in the subduction context. b) DEM of the Somma-Vesuvius volcanic complex (Vilardo et al., 2008) with the Mt. Somma caldera boundary (Cioni et al., 1999). The regional faults (thick dashed lines), the main faults (dashed lines) and the 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.

The present-day Mt. Somma caldera boundary shows a substantial difference between its northern and southern sectors (Fig. 1b). In particular, 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 corresponds 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 Vesuvius edifice (Fron dini et al., 2004; Granieri et al., 2013). In addition, this intersection also separates the southwest crater area from the rest of the crater highlighting an elevation discrepancy (i.e. ~120 m) in favour of the northeast sector of Vesuvius, which features the summit at 1,281 m above sea level (a.s.l.).

3.1. The 1631 sub-Plinian eruption

In 1631, a sub-Plinian eruption affected the structural setting of Vesuvius 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 mentioned that before the 1631 eruption, the Vesuvius summit was ~55 m higher than Mt. Somma, with a crater of ~1,500 m and ~480 m in circumference and diameter, respectively. These dimensions increased respectively to ~5,230 m and ~1,690 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 impact of the 1631 eruption on the Vesuvius morphology. It is worth noting 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 (Figs. 2a and 2b), 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 Figs. 2a and 2b).

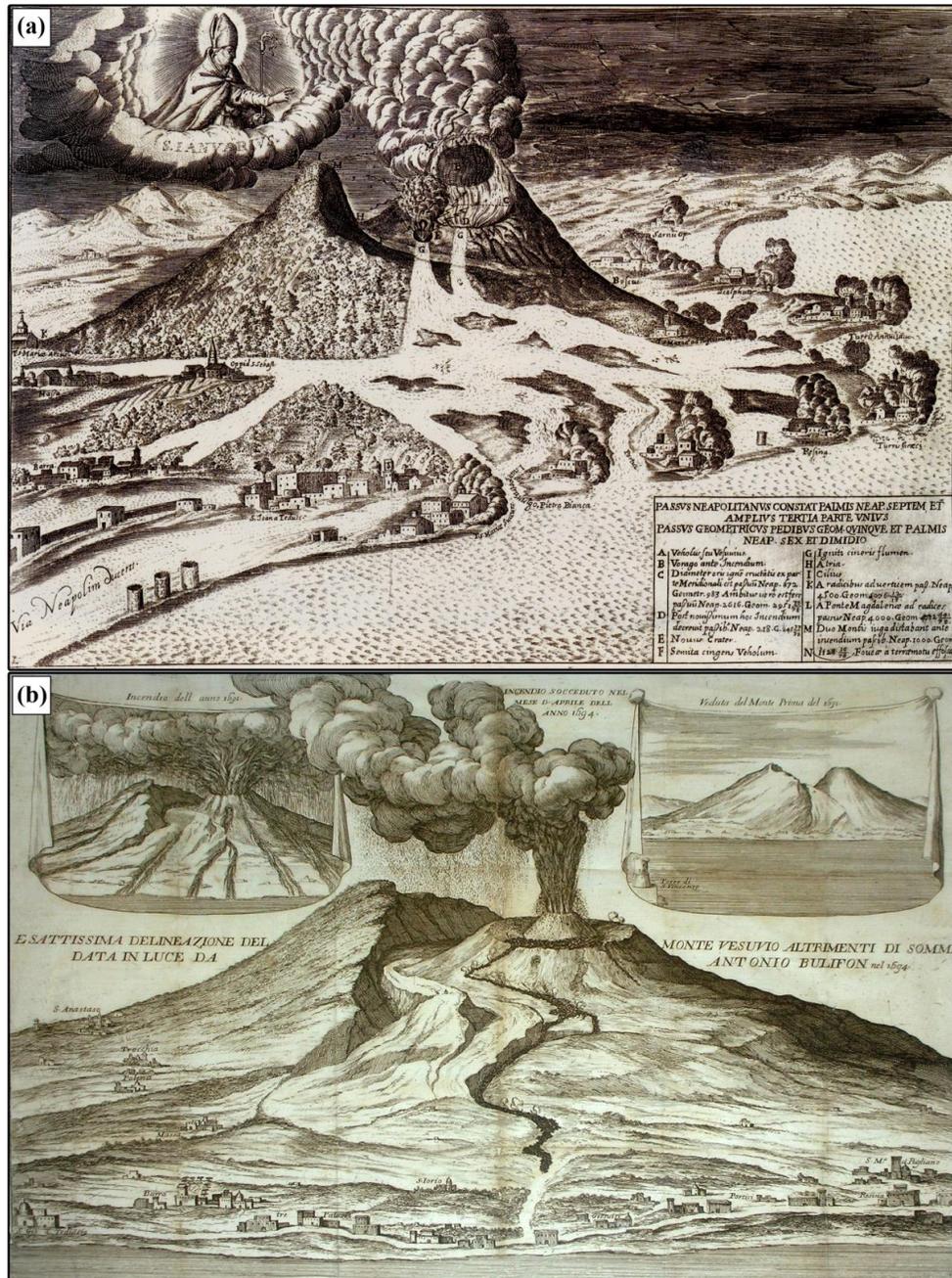


Figure 2: a) Painting from “Palazzo Reale” (see Fig. 1c) of Somma-Vesuvius after the 1631 eruption (Carafa, 1632). The letters refer to Carafa’s measurements for characterizing the 1631 caldera (legend in the lower right). b) Painting of Somma-Vesuvius showing the 1694 eruption (Bulifon, 1694) and the 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.

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 accompanied by seismic shocks and ash fallout in the Neapolitan area. First, a 5-minutes earthquake occurred, which accompanied the collapse of the caldera. 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 2,000 m followed by a 5-m high tsunami. Such observations were painted by Scipione Compagno (Guidoboni, 2008). Pyroclastic flows started simultaneously with the caldera-forming collapse (Rosi et al., 1993). However, 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 documented 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 observations reported an elevation drop of the new Vesuvius summit below the Mt. Somma top, with caldera dimension clearly greater than the crater 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 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 eruption (DPC, 2015).

3.2. Observations from literature

In terms of morphological observations of the 1631 eruption, a critical review of the available literature highlights significant differences relative to the circumference (C) and diameter (D) of the crater produced 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 authors, which ranges from ~1,682 to 2,949 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 1,853 m for the *PN* and *MI*, respectively). Although most of the authors assessed C only (Table 1), Carafa (1632) and Masculo (1633) measured both C and D . It follows 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 more than 1,000 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 reliable. Accordingly to the detailed description of the 1631 eruption features, also consistent with the reconstruction of Rosi et al. (1993), the data provided by Carafa (1632; label 1 in Fig. 3) have been taken as reference for performing a comparative analysis with the results of this investigation.

Year	Diameter (D)			Circumference (C)			References
	Value	Unit	Value in m	Value	Unit	Value in m	
1632	872	<i>PN</i>	1,686	2,703	<i>PN</i>	5,225	Carafa, 1632 ⁽¹⁾
1632	—	—	2,359 *	4	<i>MI</i>	7,412	Braccini, 1631, 1632 ⁽²⁾
1633	870	<i>PN</i>	1,682	2,730	<i>PN</i>	5,277	Masculo, 1633 ⁽³⁾
1644	—	<i>PN</i>	1,769 *	3	<i>MI</i>	5,559	Evelyn, 1644 ⁽⁴⁾
1648	—	—	1,769 *	3	<i>MI</i>	5,559	Raymond, 1648 ⁽⁵⁾
1663	—	<i>PN</i>	1,769 *	3	<i>MI</i>	5,559	Magalotti, 1779 ⁽⁶⁾
1685	—	<i>PN</i>	2,359 *	4	<i>MI</i>	7,412	Burnet, 1699 ⁽⁷⁾
1695	—	—	2,359 *	4	<i>MI</i>	7,412	Drummond, 1845 ⁽⁸⁾
1734	—	<i>PN</i>	2,949 *	5	<i>MI</i>	9,265	Sorrentino, 1734 ⁽⁹⁾

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.

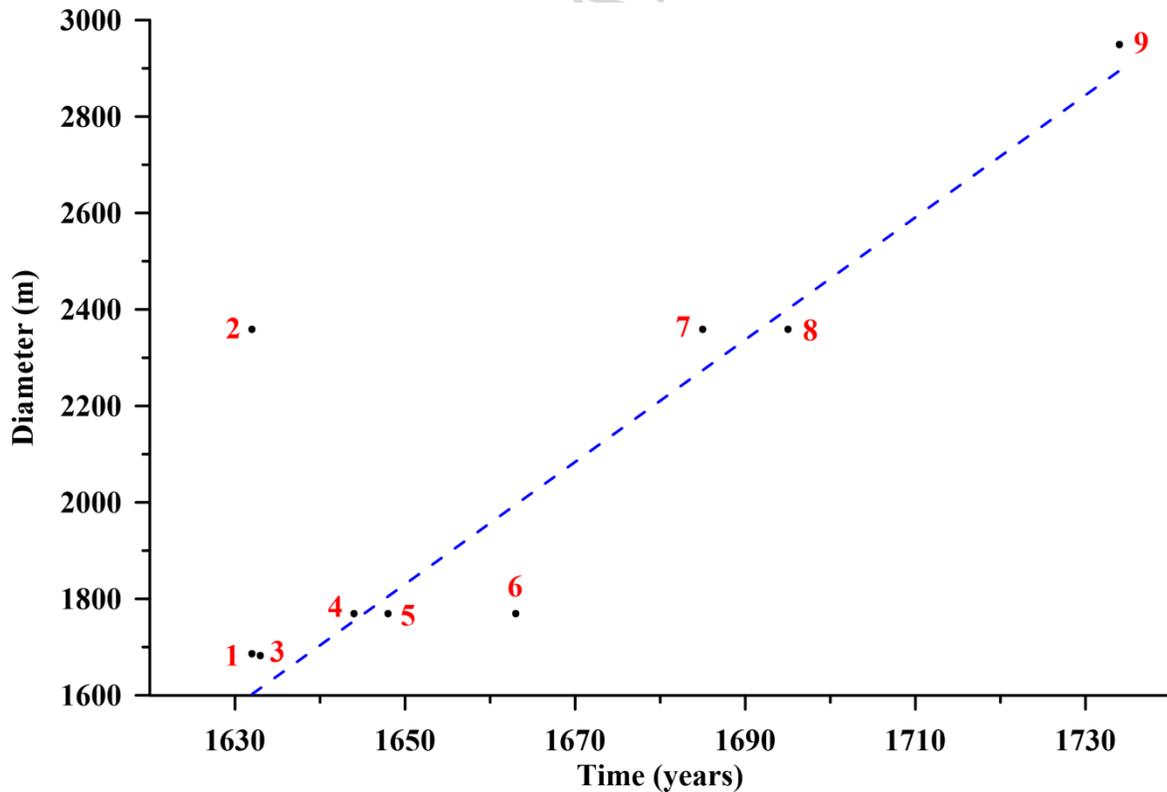


Figure 3: Measurements of the 1631 caldera diameter from literature. The blue dashed line represents the linear regression of diameter measurements, excluding the label 2 (see Sect. 3.1). Red numbers refer to the references presented in Table 1 (see numbers in brackets in the References column).

4. Data acquisition and methodology

A total of 3,949 measurements were carried out during two extensive one-month field campaigns: 1) in July 2001 on the Vesuvius cone (1,668 measurements, 20 m spacing; see Fig. 4a) and 2) in July 2003 in the lowermost part of the edifice including Mt. Somma area and also the profile going down into the actual Vesuvius crater (2,281 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 CO₂ 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 measurements, 20 m spacing) was added to achieved covering the western lower flank of the Vesuvius cone increasing the total amount of measurements up to 4,018. 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 measurement was georeferenced 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 circular profiles 1) along the 1944 crater rim, 2) at the base of the Vesuvius cone, and 3) the largest and topographically lowermost one that includes 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. CO₂ concentration was measured by injecting the samples into two infrared spectrometers. The high variability of CO₂ concentration, as expected for dormant volcanoes and surrounding areas, motivated the use of two spectrometers. One spectrometer was used to detect and measure low concentrations (< 3000 ppm), while the other is set for higher concentrations (i.e. 3,000–100,000 ppm). The analytical uncertainty related to the CO₂ concentration retrieval is estimated at ± 5% (Finizola et al., 2009).

Considering the uneven distribution of the data (2001 and 2003 campaigns), we produced the CO₂ 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. 200×200 m). Then, the resulting interpolation was integrated into the data for locally interpolating at higher resolution (40×40 m). The largest areas with no data were blanked.

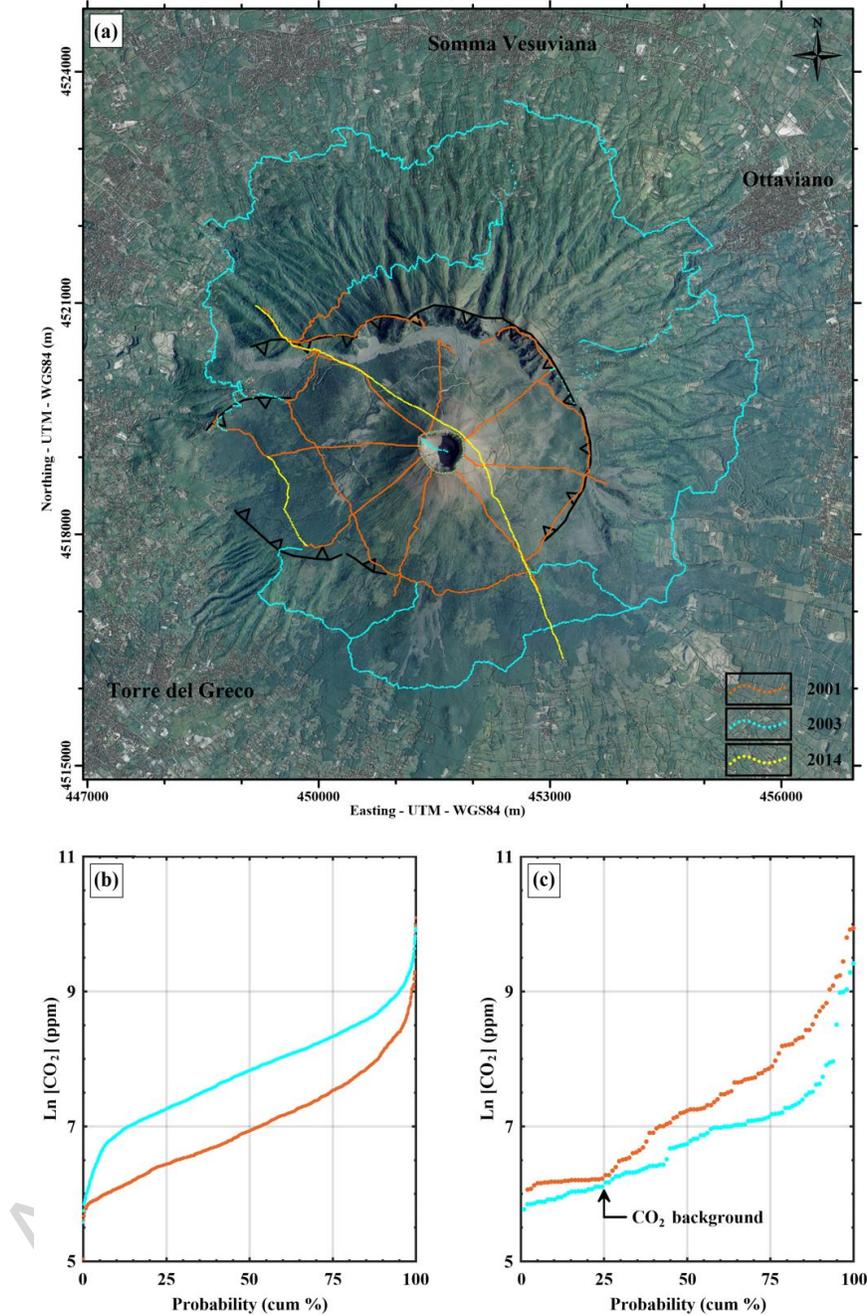


Figure 4: (a) Location of the soil CO₂ concentration measurements performed on July 2001, July 2003 and March 2014 on the Somma-Vesuvius volcanic complex; (b) Probability plot technique (Sinclair, 1974) performed on the 2001 (orange) and 2003 (cyan) soil CO₂ concentration data acquired on the entire volcanic complex; (c) Probability plot technique (Sinclair, 1974) performed on the 2001 (orange) and 2003 (cyan) soil CO₂ concentration data acquired on the reiteration profile located on the crater rim (98 measurements; see Fig. 4a). The CO₂ background of the Somma-Vesuvius volcanic complex, obtained through the probability plot technique, is estimated around 550 ppm.

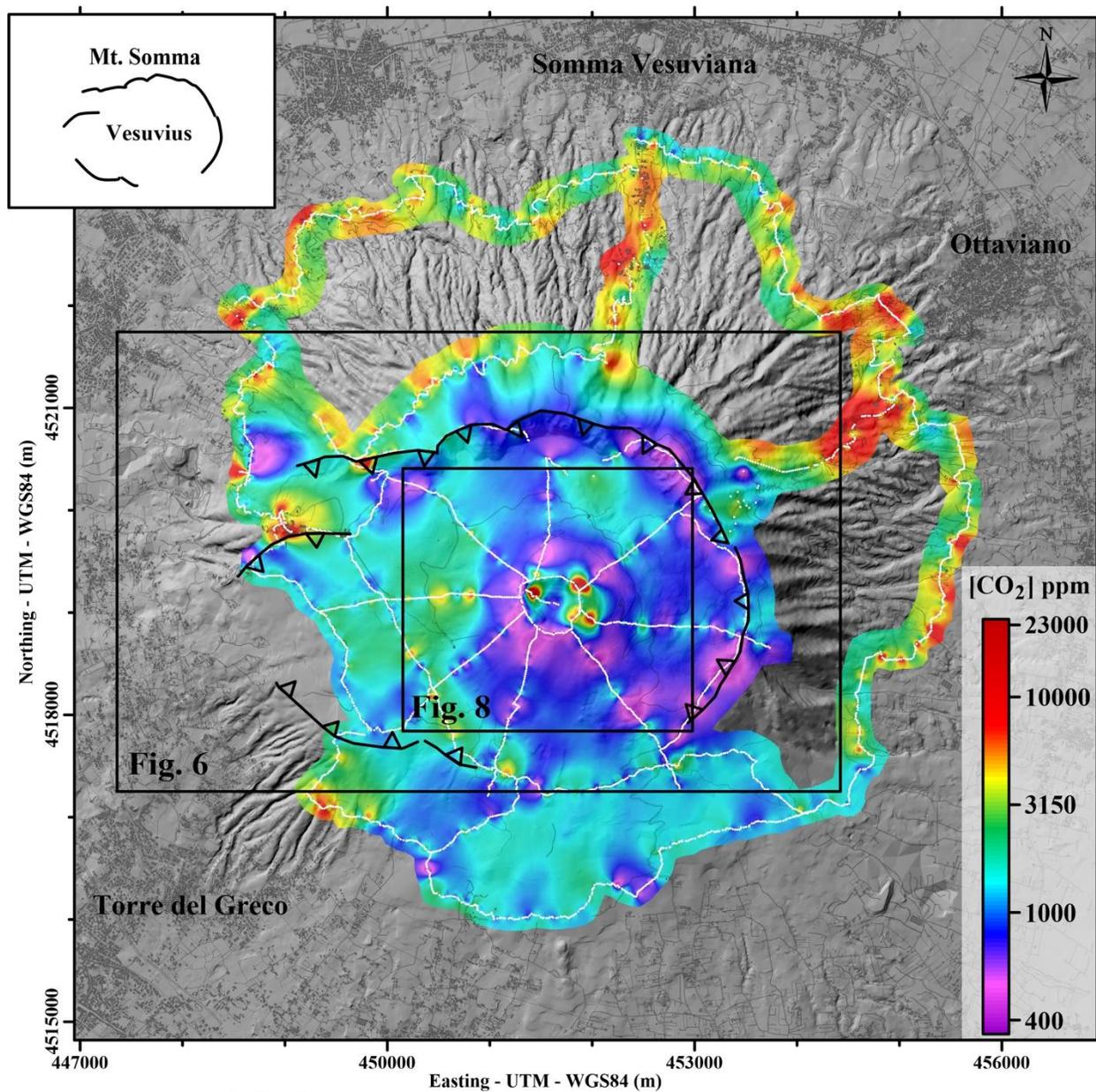


Figure 5: Soil CO₂ concentration map of the Somma-Vesuvius volcanic complex. White dots show the CO₂ measurements. The reported Mt. Somma caldera limit (line with triangles) is extracted from Cioni et al. (1999). The rectangles localize the extension of Figs. 6 and 8.

5. Results and discussion

Before discussing the soil CO₂ 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 CO₂ 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 result is attributed to the locations of the 2003 measurements on the northern flank of Mt. Somma, where dense forests cover investigated area. Then, we also tested the probability plot technique on the 98 CO₂ measurements collected along the 1944 crater rim during both campaigns. The result displays a significant decrease in soil CO₂ concentration between 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.

5.1 Soil CO₂ concentration on the Somma-Vesuvius volcanic complex

The soil CO₂ 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 characterised by CO₂ concentrations close to 1,000,000 ppm (i.e. 100% in volume).

Figure 5 highlights the areal distribution and the high heterogeneity of the soil CO₂ 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 CO₂ concentration 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 CO₂ background values below 1,000 ppm with scattered CO₂ peaks; 3) the area located outside the Mt. Somma caldera (i.e. N, E, and W flanks), having CO₂ values in average 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 CO₂ issued from deep degassing (i.e. volcanic origin) or produced by “soil respiration” (i.e. biogenic origin; Mielnick and Dugas, 2000; Aiuppa et al., 2004). Indeed, by comparing Fig. 5 with

Fig. 1b we observe that sector 3 is dominated by a dense forest being responsible of the abundant presence of CO₂. As a consequence, 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 intensive in terms of soil CO₂ concentrations, this is also the case of the bottom of the inner part of the Mt. Somma caldera (i.e. sector 2). In contrast, sector 1 has almost no vegetation but shows localized CO₂ anomalies 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 CO₂ degassing over the entire volcanic edifice, weak, moderate, and strong degassing areas can be observed, accordingly to other volcanoes (e.g. Galeras, Poas and Rincon 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 suggested for the Somma-Vesuvius.

5.2 Soil CO₂ concentration on the flanks of the Vesuvius cone

Figure 6 shows that CO₂ anomalies located near the present-day summit area of Vesuvius are well constrained within the 1906 crater boundary, showing significant CO₂ 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 CO₂ 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 CO₂ peaks around the summit area together with the distribution and location 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 mentioned in Section 2 (Fig. 1b).

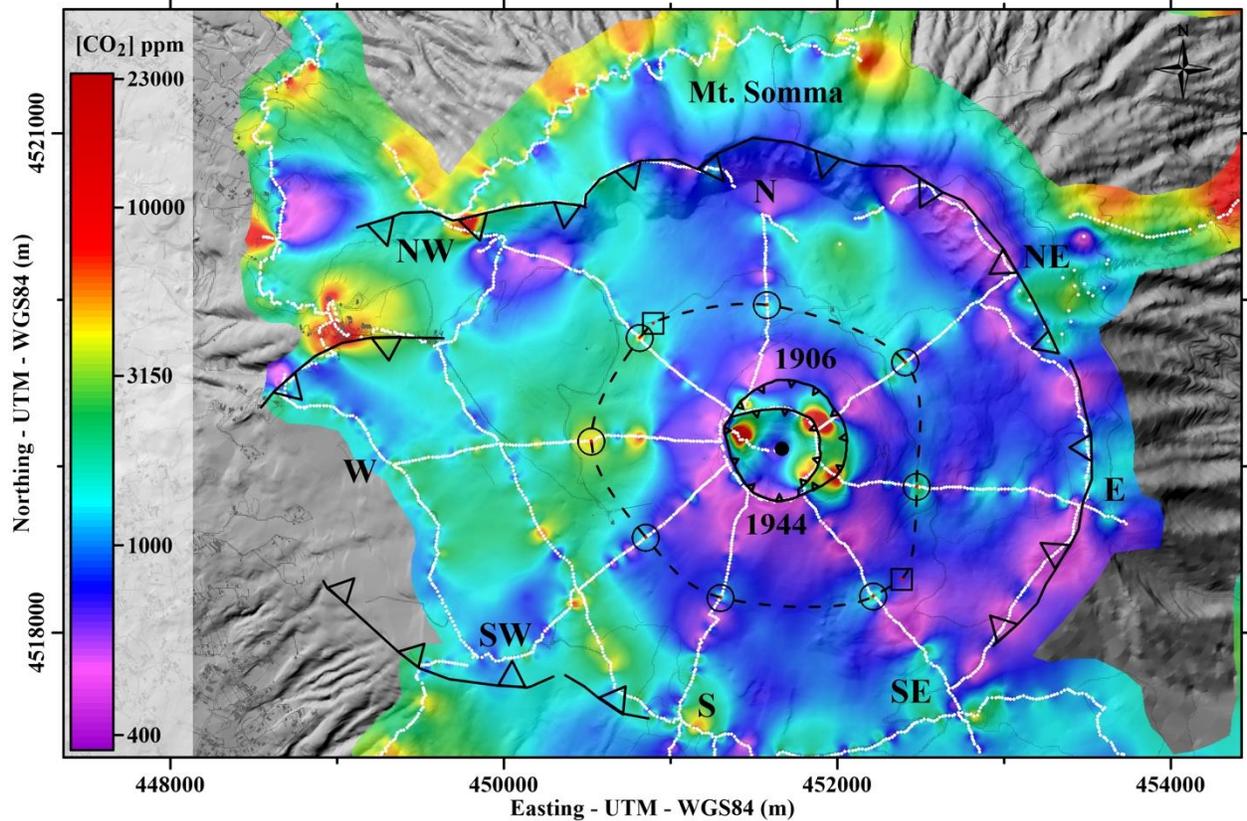


Figure 6: Soil CO₂ concentration map. Circles refer to the CO₂ peaks identified along the 8 radial profiles while squares refer to the NW-SE profile (Poret et al., 2016; details in Table 2). Mt. Somma caldera rim is from Cioni et al., 1999. The 1906 and 1944 crater rims are from Andronico et al., 1995; Santacroce and Sbrana, 2003. Black dot shows the bottom of the 1944 crater.

Comparing the identified CO₂ anomalous peaks (Fig. 6) with the previous studies (Fron dini 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 CO₂ anomalous peaks (see Fig. 1a therein), and measurements of Fron dini 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).

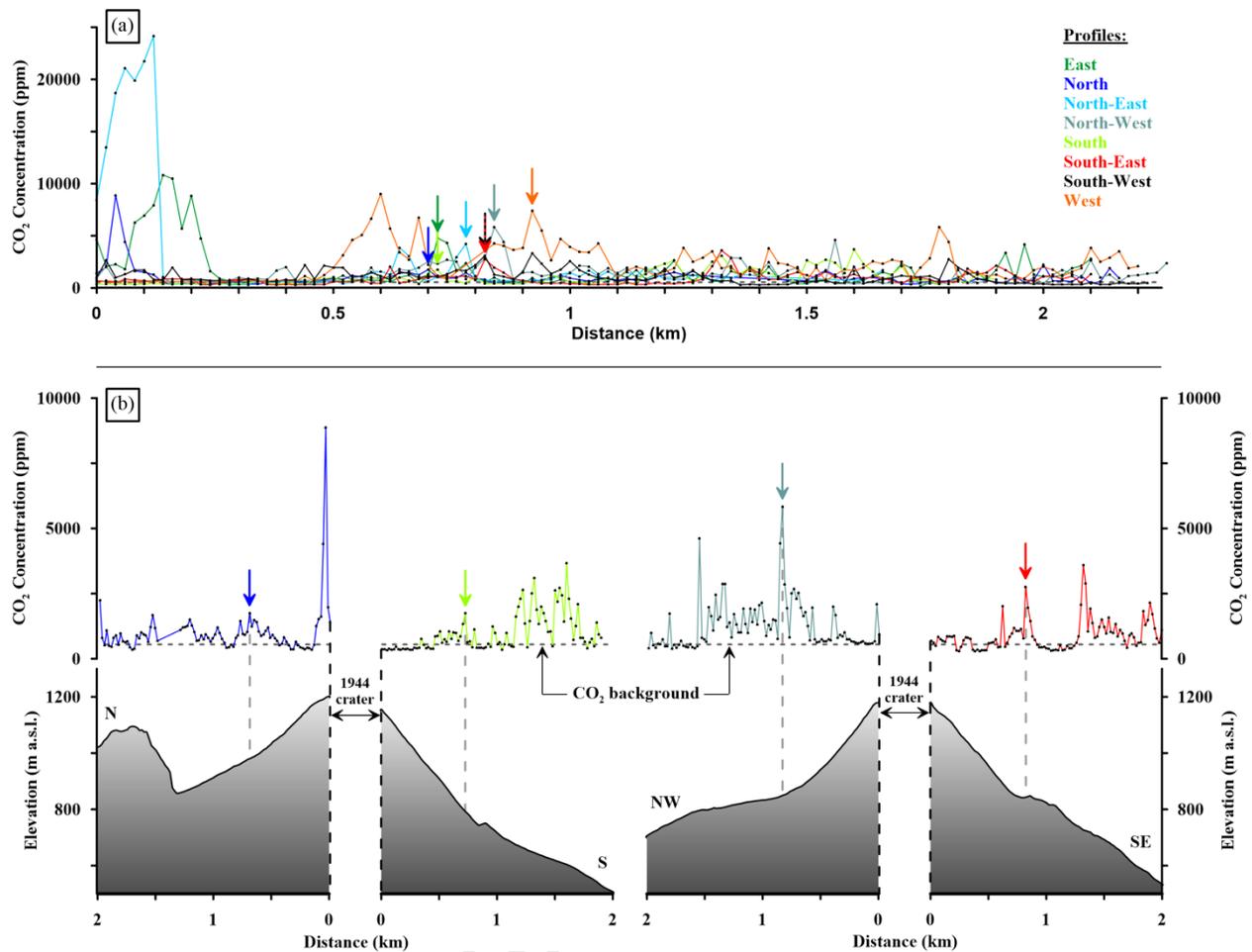


Figure 7: a) Soil CO₂ concentration profiles measured on the Vesuvius cone. Distance is set from the top of the actual crater rim towards the base of the cone. The arrows refer to the CO₂ peaks described in Table 2. The CO₂ background for the Vesuvius cone, 550 ppm, was identified by means of the probability plot method (Sinclair, 1974). b) Example of the N-S and NW-SE CO₂ concentration profiles with the corresponding topography.

In particular, by analysing the 8 profiles from the 1944 crater rim towards the base of the cone shows a systematic local CO₂ increase (arrows in Fig. 7a). The CO₂ concentration peaks range between 1,426 and 7,410 ppm (Table 2). In addition, the same CO₂ anomalies were observed 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 CO₂ 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). 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).

Id	Longitude UTM WGS 84	Latitude UTM WGS 84	[CO₂] (ppm)	Altitude (m a.s.l.)	Distance from the 1944 crater rim (m)	Distance from the bottom of 1944 crater (m)
N	451579	4519969	1749	975	675	869
NE	452406	4519627	4224	933	751	903
E	452475	4518878	4776	950	694	838
SE	452215	4518219	2766	840	873	1041
S	451300	4518212	1748	790	735	966
SW	450851	4518573	1426	791	747	976
W	450524	4519150	7410	797	847	1146
NW	450814	4519772	5826	845	790	1084
NW14	450894	4519861	2449	848	804	1082
SE14	452386	4518321	2024	844	827	1063

Table 2: Location of the 10 CO₂ concentration peaks identified on each radial profile with the corresponding CO₂ concentration value, elevation, horizontal distance from the 1944 crater rim, and horizontal distance from the bottom of the 1944 crater.

The circular shape of the observed CO₂ 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 CO₂ concentration (Table 2). Furthermore, the elevation of the CO₂ peaks varies within less than 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 ~1,146 m. The rather symmetric shape observed through the CO₂ anomalies indicates an average diameter of ~1,956 m near the base of the Vesuvius cone.

The circular shape from the identified CO₂ peaks (hereinafter “CO₂ 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 ~1,686 m diameter (Table 1), appears to be similar to the CO₂ limit. We quantitatively compared the CO₂ limit with

the inferred 1631 caldera boundary (Carafa, 1632), which are both displayed in Fig. 8. Considering 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 present 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 CO₂ limit (Fig. 8) illustrates such an irregular shape, which could not be observed by Carafa (1632) from his viewpoint (Fig. 1c). Considering a non-perfectly circular boundary, the average diameter of the CO₂ limit deriving from the anomalous values is 1,956 m ($\sigma = 129$ m), having the largest diameter (~2,125 m) oriented north-west-south-eastwards, and the shortest one (i.e. ~1,834 m) along the north-south profile.

The 1631 caldera boundaries from Carafa (1632) and the CO₂ 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 qualitative due to the large uncertainties in both methods. Indeed, by calculating 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 CO₂ concentration survey suffers from uncertainties relative to the soil permeability that partially controls the soil CO₂ concentration. Moreover, fracture orientations drive CO₂ 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.

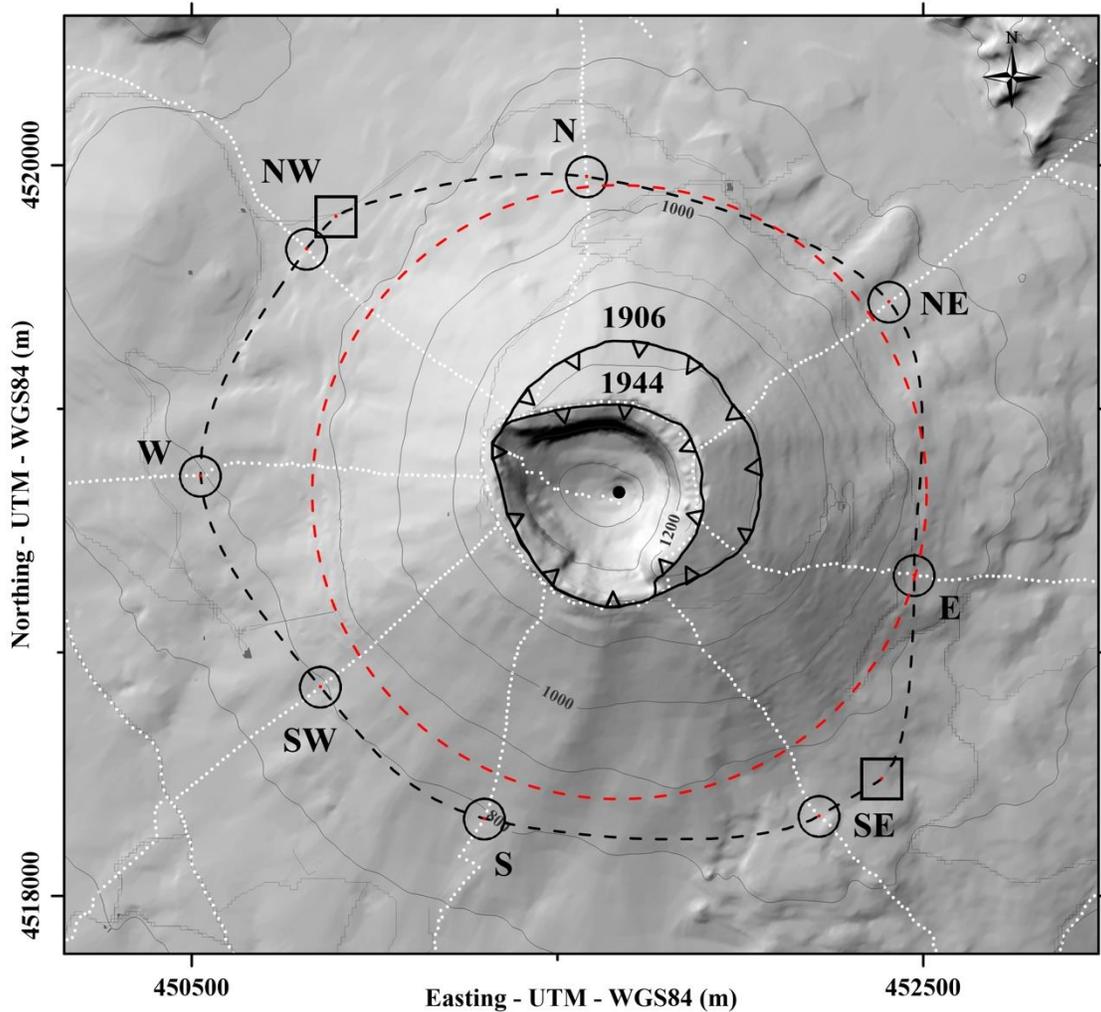


Figure 8: Comparison between the 1631 caldera (Carafa, 1632) and the CO₂ limit. Circles refer to the CO₂ peaks identified along the 8 radial profiles, while squares refer to the NW-SE profile (Poret et al., 2016; see Table 2). Red dashed line is the 1631 caldera boundary (from Carafa, 1632, and Rosi et al., 1993) and the black dashed line is the limit inferred from the CO₂ concentration peaks. Black dot shows the bottom of 1944 crater.

In Fig. 6, the west flank of the Vesuvius cone shows two CO₂ 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 CO₂ results were also compared with those of a 3-D density model obtained from a recent gravity survey (Linde et al., 2017). Figure 9 shows the overlapping of the CO₂ limit with two horizontal density slices at 800–900 m and 700–800 m a.s.l. (respectively Figs. 9a and 9b). The two elevation intervals are motivated by the CO₂ peak elevations (Table 2). Indeed, the average elevation of the CO₂ limit is 865 m a.s.l.. The two elevation intervals were therefore chosen for embracing both the average elevation of the supposed 1631 caldera rim as well as its buried structure. The comparison between CO₂ 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/m³) inside the 1631 caldera boundary defined by the CO₂ limit, suggesting that the 1631 caldera was refilled by volcanic products that are less dense than the outer and older part of the Vesuvius cone. These gravimetric results clearly show that the 1631 eruption 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 CO₂ limit defines the 1631 caldera boundary.

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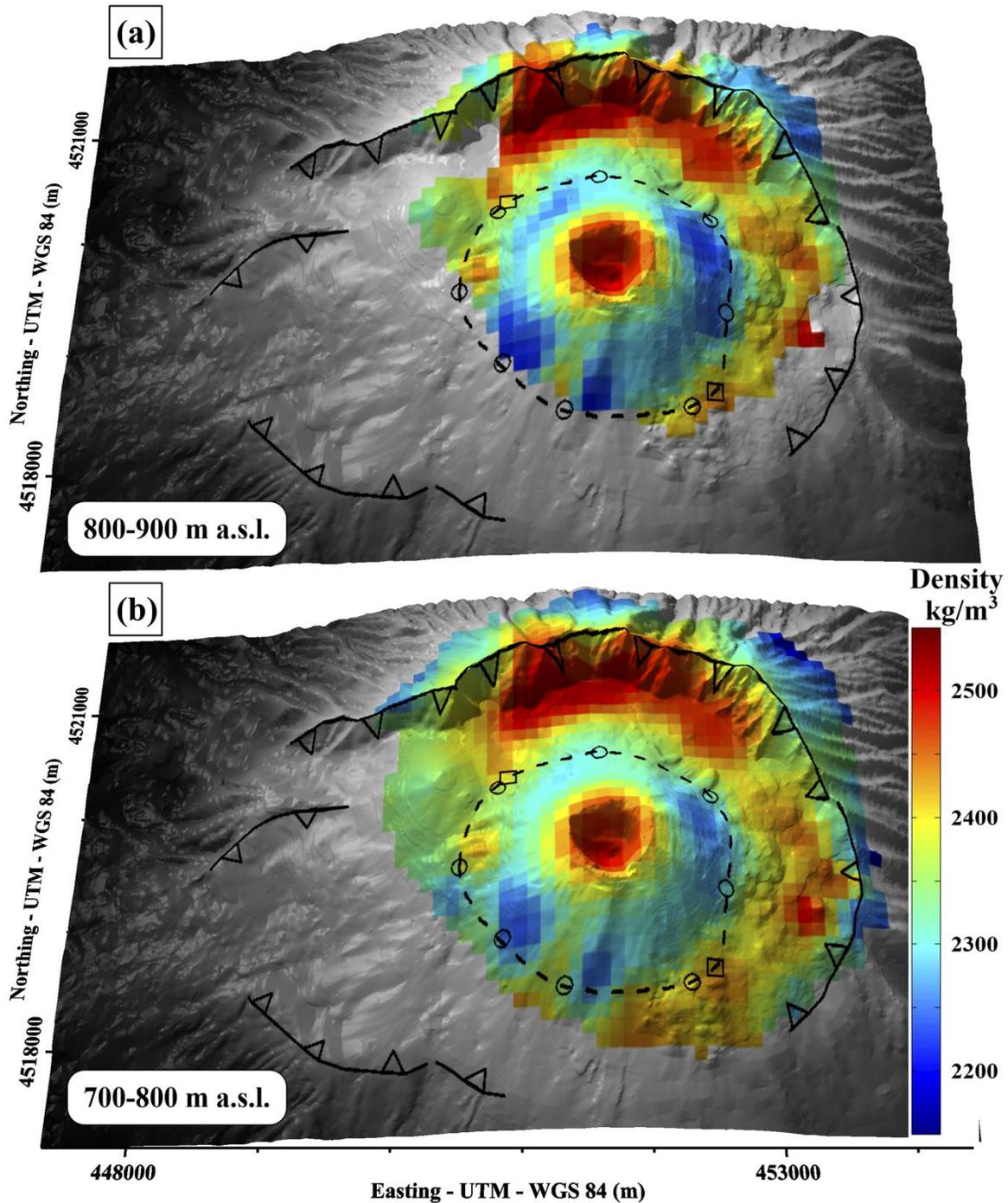


Figure 9: 3-D view of the Somma-Vesuvius displaying the density model and the CO₂ peaks and limit (details in Fig. 7 and Table 2). a) Comparison between the limit defined by the CO₂ peaks with a horizontal density slice between 800 and 900 m a.s.l.; b) The same comparison but for a horizontal density slice between 700 and 800 m a.s.l.. Circles refer to the CO₂ 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.

6. Conclusions

We have carried out 4,018 soil CO₂ measurements along profiles covering the whole Somma-Vesuvius volcanic complex (50 km²) 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 Vesuvius cone with the highest CO₂ concentration value (~24,140 ppm) located inside the partially buried 1906 crater rim, 2) the flanks of the Vesuvius cone characterized by weak CO₂ concentrations, and 3) the area located outside Mt. Somma caldera with moderate CO₂ concentrations. This study focuses on the short spatial extension anomalies measured on the flanks of the Vesuvius cone. The CO₂ data revealed a roughly circular degassing structure located between 790 and 975 m a.s.l.. This CO₂ limit was compared with a review of the historical literature available showing similar dimensions of the 1631 caldera boundary (i.e. diameter of ~1,686 m). The quantitative analysis indicates radial discrepancies 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 CO₂ 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 CO₂ 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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Highlights

- 1 More than 4000 soil CO₂ measurements over the Somma-Vesuvius volcanic edifice (>50 km²).
- 2 Production of the soil CO₂ concentration map over the domain at very high spatial resolution (40 m).
- 3 Benefiting of the 20-m step measurement for identifying the main structural elements.
- 4 Local CO₂ maxima on each radial profile lead to characterize a circular boundary coinciding with the caldera produced by the 1631 sub-Plinian eruption.

ACCEPTED MANUSCRIPT