



# Carbon isotopic signature of interstitial soil gases reveals the potential role of ecosystems in mitigating geogenic greenhouse gas emissions: Case studies from hydrothermal systems in Italy

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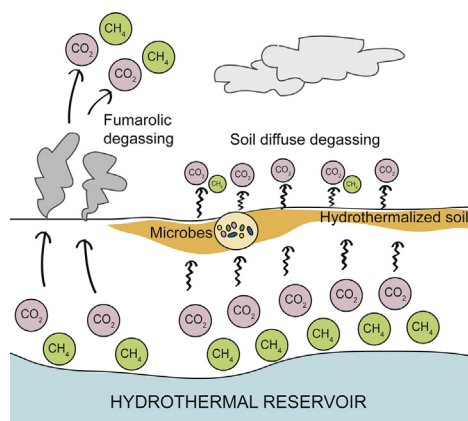
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## HIGHLIGHTS

- Greenhouse gases are released from hydrothermal systems through diffuse degassing.
- Carbon in CO<sub>2</sub> from soil gases is isotopically heavier than that from fumaroles.
- CO<sub>2</sub>/CH<sub>4</sub> ratios in soil gases are higher than those measured in fumarolic emissions.
- Autotrophs and methanotrophs mitigate the release of geogenic greenhouse gases.
- Microbes contribute to regulate CH<sub>4</sub> (and CO<sub>2</sub>) emissions from hydrothermal areas.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Volcanic and hydrothermal areas largely contribute to the natural emission of greenhouse gases to the atmosphere, although large uncertainties in estimating their global output still remain. Nevertheless, CO<sub>2</sub> and CH<sub>4</sub> discharged from hydrothermal fluid reservoirs may support active soil microbial communities. Such secondary processes can control and reduce the flux of these gases to the atmosphere. In order to evaluate the effects deriving from the presence of microbial activity, chemical and carbon (in CO<sub>2</sub> and CH<sub>4</sub>) isotopic composition of interstitial soil gases, as well as diffuse CO<sub>2</sub> fluxes, of three hydrothermal systems from Italy were investigated, i.e. (i) Solfatarata crater (Campi Flegrei), (ii) Monterotondo Marittimo (Larderello geothermal field) and (iii) Baia di Levante in Vulcano Island (Aeolian Archipelago), where soil CO<sub>2</sub> fluxes up to 2400, 1920 and 346 g m<sup>-2</sup> day<sup>-1</sup> were measured, respectively. Despite the large supply of hydrothermal fluids, <sup>13</sup>C<sub>2</sub> enrichments were observed in interstitial soil gases with respect to the fumarolic gas discharges, pointing to the occurrence of autotrophic CO<sub>2</sub> fixation processes during the migration of deep-sourced fluids towards the soil-air interface. On the other hand, (i) the δ<sup>13</sup>C-CH<sub>4</sub> values (up to -48‰ vs. V-PDB higher than those measured at the fumarolic emissions) of the interstitial soil gases and (ii) the comparison of the CO<sub>2</sub>/CH<sub>4</sub> ratios between soil gases and fumarolic

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emissions suggested that the deep-sourced CH<sub>4</sub> was partly consumed by methanotrophic activity, as supported by isotope fractionation modeling. These findings confirmed the key role that methanotrophs play in mitigating the release of geogenic greenhouse gases from volcanic and hydrothermal environments.

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## 1. Introduction

Carbon dioxide and methane are considered among the main greenhouse gases responsible for the current global warming (e.g. IPCC, 2007a). Concentrations of these gases in the atmosphere have roughly doubled since the late 18th century (Ciais et al., 2013), reaching 404 ppmv and 1859 ppbv in October 2018, respectively (data from the NOAA/ESRL Global Monitoring Division; [www.esrl.noaa.gov/gmd](http://www.esrl.noaa.gov/gmd)). Whilst the main reason for the rapid increment in the low atmosphere of CO<sub>2</sub> and CH<sub>4</sub> must be sought in anthropogenic activities related to the massive exploitation (and burning) of fossil fuels since the beginning of the industrial era, their quantification from natural sources at a global scale still suffers from large degrees of uncertainty (e.g. Burton et al., 2013; Mörner and Etiope, 2002). Among geogenic sources, degassing from volcanic and associated hydrothermal areas is responsible for a large fraction of the natural CO<sub>2</sub> emissions (e.g. Holloway et al., 2007), with a global subaerial volcanic CO<sub>2</sub> flux estimated at  $540 \times 10^{12}$  g/yr (Burton et al., 2013). Carbon dioxide discharged from fumarolic vents and diffuse soil degassing was recognized as an important mechanism for gas release from volcanoes (Mörner and Etiope, 2002), which at a local scale may exceed that emitted from volcanic plumes (e.g. Baubron et al., 1991; Chiodini et al., 1998; Italiano et al., 1998). Areas characterized by intense diffuse degassing significantly (and persistently) contribute to the total gas emissions from volcanic/hydrothermal systems (Cardellini et al., 2003; Chiodini et al., 2004; Granieri et al., 2010; Tassi et al., 2013; Viveiros et al., 2010), with associated CO<sub>2</sub> fluxes that are often larger than those related to the fumarolic vents occurring in the same areas (e.g. D'Alessandro et al., 2006; Pecoraino et al., 2005; Chiodini et al., 2010; Aiuppa et al., 2013).

Despite the fact that the Global Warming Potential (GWP) of CH<sub>4</sub> is 25 times higher than that of CO<sub>2</sub> (IPCC, 2007b), the global CH<sub>4</sub> output from volcanic and hydrothermal areas is still largely unknown (Mörner and Etiope, 2002). In general, whilst contributions from the biosphere to atmospheric CH<sub>4</sub> are relatively well characterized, accounting for  $345 \times 10^{12}$  g CH<sub>4</sub>/yr (Etiope and Klusman, 2002), few data are available for those released from geogenic sources, which, according to Etiope and Klusman (2002), should account for 30–70  $\times 10^{12}$  g CH<sub>4</sub>/yr. Geogenic CH<sub>4</sub> contributions are expected to be relevant within peculiar geological settings (e.g. Cardellini et al., 2003; Castaldi and Tedesco, 2005; D'Alessandro et al., 2009, 2011; Tassi et al., 2013, 2015a), such as those that characterize the Italian peninsula, where the numerous volcanic and hydrothermal areas discharge up to  $0.043 \times 10^{12}$  g CH<sub>4</sub>/yr (Etiope et al., 2007), i.e. an amount comparable to that emitted from the European geothermal areas (about  $10^{11}$  g CH<sub>4</sub>/yr). Nevertheless, the CO<sub>2</sub>/CH<sub>4</sub> ratio from diffuse degassing is generally higher than that measured in the fumarolic discharges from the same areas, suggesting that CH<sub>4</sub> is partially lost as the deep-seated gas flows through the soil (D'Alessandro et al., 2009).

Soil is considered the largest biological sink for atmospheric CH<sub>4</sub>, responsible for a global uptake of about  $22 \times 10^{12}$  g CH<sub>4</sub>/yr (Dutaur and Verchot, 2007). More than 50% of CH<sub>4</sub> permeating the soil is consumed by methanotrophs before being emitted to the atmosphere (Reeburgh, 2003). These bacteria use CH<sub>4</sub> as energy source producing CO<sub>2</sub> (e.g. Conrad, 1996; Hanson and Hanson, 1996; Op den Camp et al., 2009). Until ten years ago, all the known species of methanotrophs were affiliated to the bacterial phylum *Proteobacteria*, in the classes Gamma- and Alpha-proteobacteria, which, being characterized by an optimum growth temperature below 60 °C and pH >4 (Op den Camp et al., 2009 and references therein), were not expected to thrive in hot and acidic

conditions occurring in soils from volcanic and hydrothermal areas. Nevertheless, CH<sub>4</sub> oxidation in laboratory tests on soils from Solfatara crater (southern Italy) with pH down to 1.8 suggested the occurrence of methanotrophic activity even under hotter (up to 70 °C) and more acidic conditions (Castaldi and Tedesco, 2005). Finally, in 2007–2008, non-proteobacterial thermoacidophilic methanotrophs, belonging to the phylum *Verrucomicrobia*, were identified in soils and acidic hot springs from hydrothermal areas (Dunfield et al., 2007; Islam et al., 2008; Pol et al., 2007). Recent studies highlighted the presence of methanotrophic microbial communities in volcanic and hydrothermal soils based on microbiological analyses (e.g. Gagliano et al., 2014, 2016; Sharp et al., 2014) and novel species were identified able to thrive under a variety of harsh conditions, suggesting that methanotrophs likely have a wider distribution in hydrothermal environments than that previously supposed (e.g. Carere et al., 2017; van Teeseling et al., 2014). Accordingly, methanotrophic activity in hydrothermal soils was inferred on the basis of geochemical tracers, such as soil CO<sub>2</sub> and CH<sub>4</sub> flux measurements and chemical and isotopic analysis of interstitial soil gases (e.g. Castaldi and Tedesco, 2005; D'Alessandro et al., 2009, 2011; Tassi et al., 2015b).

On the other hand, both field and experimental studies (e.g. Beulig et al., 2015; Khadem et al., 2011; Nowak et al., 2015; Oppermann et al., 2010) suggested that high CO<sub>2</sub> concentrations, such as those characterizing soil gases in diffuse degassing areas, may favor microbial carbon fixation via autotrophic pathways, leading to a significant incorporation of geogenic CO<sub>2</sub> into the microbial carbon pool. The capability of microbes to incorporate CO<sub>2</sub> and oxidize CH<sub>4</sub> in the soil system before these gases are released to the atmosphere renders these communities particularly appealing in terms of bioremediation technologies and mitigation of greenhouse gas emissions (e.g. Farhan Ul Haque et al., 2018; Oppermann et al., 2010; Semrau, 2011; Strong et al., 2015; Trotsenko et al., 2009). Since microbiological investigations are generally quite expensive, extensive sampling surveys are rarely carried out. Geochemical tracers offer the opportunity to widen our knowledge on the distribution and effectiveness of microbial consumption of greenhouse gases in soils affected by geogenic CO<sub>2</sub> and CH<sub>4</sub> fluxes in natural environments.

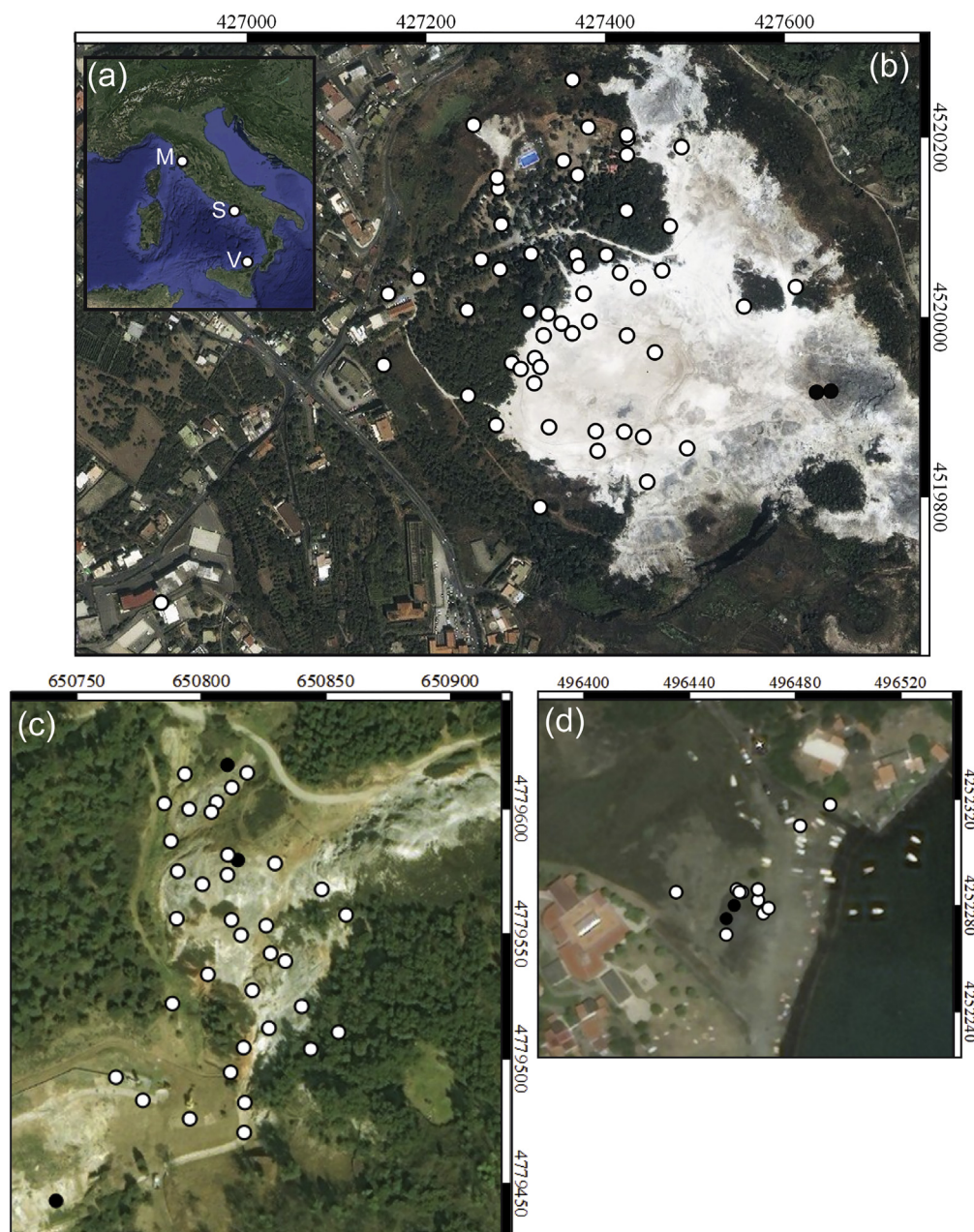
In this paper, we reported (i) soil CO<sub>2</sub> flux measurements, (ii) chemical analysis of interstitial soil gases, and (iii) carbon isotopic analysis of interstitial soil CO<sub>2</sub> and CH<sub>4</sub> carried out in three hydrothermal systems from southern and central Italy, i.e. Solfatara crater (Campi Flegrei, Naples), Monterotondo Marittimo (within the Larderello geothermal field, Tuscany), and Baia di Levante at Vulcano Island (Aeolian Archipelago). The main aim was to investigate the contribution of these diffuse degassing areas to the output of greenhouse gases and the potential role that the soil ecosystems can play in mitigating CO<sub>2</sub> and CH<sub>4</sub> emissions to the atmosphere.

## 2. Study areas

### 2.1. Solfatara crater

Solfatara crater is a tuff cone located NW of Naples along the Tyrrhenian coast close to the town of Pozzuoli, in southern Italy (Fig. 1a, b). It was formed about 4000 yr BP within the Campi Flegrei caldera, an active volcanic complex of about 100 km<sup>2</sup> that was built during two main eruptive events, i.e. (i) the Campanian Ignimbrite (39 ka; De Vivo et al., 2001) and (ii) the Neapolitan Yellow Tuff (14.9 ka; Deino et al., 2004). The caldera shows strong hydrothermal activity, consisting of thermal springs, steam-heated pools, and fumaroles (e.g. Caliro et al.,





**Fig. 1.** (a) Location of Solfatara crater (S), Monterotondo M.mo (M) and Vulcano Island (V) in Italy. The location of the interstitial soil (white circles) and fumarolic (black circles) gas sampling sites at (b) Solfatara crater, (c) Monterotondo M.mo and (d) Vulcano Island is shown.

2007; Chiodini et al., 2001; Passaro et al., 2016; Todesco et al., 2003; Valentino and Stanzione, 2003, 2004; Vaselli et al., 2011; Venturi et al., 2017). The Solfatara crater hosts one of the largest fumarolic discharges worldwide, mostly located in the NE and SE portions of the crater, with a related thermal energy flux of ~100 MW (Chiodini et al., 2001) and is characterized by a widespread soil diffuse degassing emitting about  $79 \times 10^6$  g CO<sub>2</sub>/day and  $1.04 \times 10^3$  g CH<sub>4</sub>/day from the hydrothermalized bottom area (Tassi et al., 2013). The central part of the Solfatara crater hosts three bubbling acidic mud pools (named *Fangaia*) fed by rainwater, steam condensation, and continuous inputs of hydrothermal gases. Eventually, Mediterranean maquis shrubland covers the Solfatara crater to NW where diffuse degassing is mainly dominated by soil respiration (Tassi et al., 2013).

The fluid source of the CO<sub>2</sub>-rich gas emissions at Solfatara crater consists of a 1.5–2 km deep column of ascending magmatic (about 26%) and hydrothermal (about 74%) fluids (e.g. Caliro et al., 2007;

Cardellini et al., 2017; Chiodini et al., 2001, 2015;) originated by (i) a degassing magma chamber at ~5 km depth (Gottsmann et al., 2006) and (ii) boiling of the overlying aquifer(s). The magmatic fluids mix with meteoric-originated hydrothermal liquids in the lowest part of the hydrothermal system (2–2.5 km depth), generating vapors at temperatures  $\geq 360$  °C and pressures of 200–250 bar (Caliro et al., 2007). Below this mixing zone, magmatic conditions, i.e. high temperatures and presence of magmatic acidic species (i.e. SO<sub>2</sub>, HCl, HF), prevail. Hydrothermal conditions dominate in the upper zone where the reduced gas species (e.g. CH<sub>4</sub> and H<sub>2</sub>S) are formed and the most acidic and oxidizing magmatic compounds are scrubbed (Caliro et al., 2007). According to Caliro et al. (2007), the central column of the ascending fluids is characterized by the presence of a separated vapor phase that moves from the high temperature injection zone to a shallow single phase gas zone at temperatures ranging from 190 to 230 °C and at 100–300 m depths.

## 2.2. Monterotondo Marittimo

Monterotondo Marittimo (hereafter, Monterotondo M.mo; Fig. 1a, c) belongs to the Larderello-Travale geothermal area that spans between the districts of Pisa and Grosseto (Tuscany, Central Italy), in the inner portion of the Apennine orogenic belt. Larderello is the largest and most important geothermal system in Italy and one of a few superheated geothermal systems in the world, together with “The Geysers” in California (Romagnoli et al., 2010). The area is characterized by (i) an anomalous heat flow (1000 mW/m<sup>2</sup>) (Baldi et al., 1995), (ii) a thermal gradient up to 300 °C/km, and (iii) the occurrence of thermal springs, acidic and boiling steam-heated pools, mud pools (here called “lagoni”), and steam vents (Duchi et al., 1986, 1992), related to the emplacement, during the Mio-Pliocene post-orogenic magmatism, of granitic intrusives (3.8–2.25 Ma; Dini et al., 2005; Gianelli and Laurenzi, 2001; Villa and Puxeddu, 1994) at depths comprised between 3 and 8 km (K-horizon bright spot; Batini et al., 2003, and references therein). The stratigraphic sequence of the Larderello-Travale area is made up of (Batini et al., 2003, and references therein): (i) Neogene (Late Miocene) and Quaternary continental to marine deposits; (ii) allochthonous Ligurian Complex l.s., consisting of Jurassic oceanic crust remnants (ophiolitic sequences, characterized by gabbros, pillow basalts and serpentinites), and a Jurassic-Eocene sedimentary cover (flysch units); (iii) a Late Triassic-Early Miocene sedimentary carbonate-evaporite sequence (Tuscan Nappe); and (iv) the Tuscan Metamorphic Complex (Permian-Triassic) that includes the upper Monticiano-Roccastrada Unit and the lower Gneiss Complex.

The Larderello geothermal field is mainly fed by meteoric waters, although thermo-metamorphic and magmatic fluids were also recognized (D'Amore and Bolognesi, 1994; Minissale, 1991). Two main geothermal reservoirs occur, as follows: (i) a shallow aquifer (500–1500 m), hosted in the Mesozoic carbonate-evaporite sequence pertaining to the Tuscan Nappe and showing a temperature of 220–260 °C and a pressure of 30–60 bar and (ii) a deep aquifer (<3000 m) within the Paleozoic metamorphic rocks at 300–350 °C and 40–70 bar (Barelli et al., 1995; Bertani et al., 2005).

## 2.3. Vulcano Island

Vulcano Island is located at the southernmost edge of the subduction-related Aeolian volcanic arc (southern Italy), in the Southern Tyrrhenian Sea (Fig. 1a). The island consists of (i) a main edifice developed during the last 130 ky through several phases of stratocone building and caldera collapses (De Astis et al., 1997; Keller, 1980) and (ii) a smaller island (Vulcanello), consisting of lavas and pyroclastic deposits, formed between 1000 and 1250 CE (Arrighi et al., 2006). La Fossa crater represents the presently active volcanic center where the last eruptive event took place in 1888–1890 (e.g. Clocchiatti et al., 1994). Fumarolic activity occurs at both La Fossa crater and the bay delimiting the eastern side of the isthmus that connects Vulcano to Vulcanello (Baia di Levante; Fig. 1d). The gas emissions at La Fossa crater show outlet temperatures up to 450 °C and a typical magmatic composition, with a dry gas fraction dominated by CO<sub>2</sub> and relatively high concentrations of SO<sub>2</sub>, H<sub>2</sub>S, HCl and HF (e.g. Capasso et al., 1997, 1999; Inguaggiato et al., 2012). The Baia di Levante subaerial and submerged fumaroles are characterized by outlet temperatures <100 °C and a typical hydrothermal composition, consisting of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S with relatively high CH<sub>4</sub> contents (Capaccioni et al., 2001), the latter two gases likely produced by interactions between deep originated fluids and a shallow aquifer (Capasso et al., 1997, 2001a; Chiodini et al., 1995). Geothermal exploratory wells drilled near Baia di Levante (AGIP-Sommaruga, 1984; Todesco, 1995) suggested the presence of the multi-layer hydrothermal system, which consists of (i) a shallow aquifer (at 7–14 m depth) at ~100 °C, (ii) an intermediate aquifer (at ~100 m depth) with a temperature of ~136 °C, and (iii) a deep aquifer at ~200 m depth and nearly ~200 °C with a seawater-like chemical composition.

## 3. Materials and methods

### 3.1. Soil CO<sub>2</sub> flux measurements

Soil CO<sub>2</sub> flux measurements were carried out following the accumulation chamber (AC) method (Chiodini et al., 1998). A cylindrical chamber (basal area 200 cm<sup>2</sup>; inner volume: 3060 cm<sup>3</sup>) was placed firmly on the ground and the gas was continuously pumped from the chamber, using a low-flux pump (20 mL/s), to an Infra-Red (IR) spectrophotometer (Licor® Li-820; measurement range: 0–20,000 ppm; accuracy: 4%). Once passed through the detector, the gas was injected back into the chamber to minimize the disturbance of the gas flux. An analog-to-digital (AD) converter allowed to visualize the increase in time of the CO<sub>2</sub> concentration inside the chamber (dC<sub>CO2</sub>/dt) on a palmtop computer equipped with a dedicated software. The CO<sub>2</sub> flux from the soil (ΦCO<sub>2</sub>) was then determined, as follows (Chiodini et al., 1998):

$$\Phi\text{CO}_2 = cf \times d\text{C}_{\text{CO}_2}/dt \quad (1)$$

where cf is a constant factor, which depends on (i) the geometry of the measuring equipment and (ii) the air temperature and pressure (Chiodini et al., 1998). The proportionality (cf) between dC<sub>CO2</sub>/dt and ΦCO<sub>2</sub> was determined by laboratory tests, during which the ΦCO<sub>2</sub> values from soil were simulated by injecting CO<sub>2</sub> at different known fluxes into the accumulation chamber. Several measurements were performed in the range from 10 to 10,000 g m<sup>-2</sup> day<sup>-1</sup> by checking the imposed flux by means of a precision flowmeter (accuracy 1.5%).

### 3.2. Sampling and analytical procedures for fumarolic fluids and interstitial soil gases

Fumarolic gases were collected by inserting a Titanium tube into the fumarolic vent and then, connected to a sampling line consisting of a series of dewared glass tubes (Vaselli et al., 2006), which conveyed the gas into (i) a pre-evacuated 60 mL glass flask, equipped with a Thorion® valve, containing a 4 M NaOH and 0.15 M Cd(OH)<sub>2</sub> suspension (Montegrossi et al., 2001), or (ii) a Graham type condenser connected, through a PTFE three-way valve, to a 12 mL Labco Exetainer® glass vial for the sampling of the dry gas fraction (Tassi et al., 2015a).

A stainless-steel tube (inner diameter 0.4 cm) was inserted at 5 to 20 cm depth to collect interstitial soil gases. The tube was then connected, through a PTFE three-way valve, to a 60 mL plastic syringe used for pumping the gas from the tube, and to (i) a 12 mL glass vial, equipped with a pierceable rubber septum (Labco Exetainer®), for chemical analyses, and (ii) a 1 L Supelco's Tedlar® gas sampling bag, equipped with a push/pull lock valve, for isotopic analyses (Tassi et al., 2015a, 2015b). Soil temperature was determined by inserting a thermocouple in the soil down to the sampling depth.

Gas analyses were carried out by Gas-Chromatography (GC) using (i) a Shimadzu 15A GC equipped with a Thermal Conductivity Detector (TCD) and either a 10 m long 5A Molecular Sieve column (for N<sub>2</sub>, O<sub>2</sub>, Ar and H<sub>2</sub> both in the headspace of the glass flasks and in the glass vials for fumarolic and interstitial soil gases, respectively), or a 3 m long column filled with 80/100 mesh Porapak Q (for CO<sub>2</sub> and H<sub>2</sub>S in the interstitial soil gases), (ii) a Shimadzu 14A GC equipped with a Flame Ionization Detector (FID) and a 10 m long stainless steel column filled with 23% SP 1700 on Chromosorb PAW (80/100 mesh) for the analysis of light hydrocarbons (C<sub>1</sub>–C<sub>3</sub>), and (iii) Thermo Trace Ultra GC coupled with a Thermo DSQ Quadrupole Mass Spectrometer (MS) for the analysis of C<sub>4+</sub> VOCs in fumarolic and soil gases. Sample injection into the GC-MS was carried out after exposing the gas samples collected in the glass vials to a 2 cm long DiVinylBenzene – Carboxen– PolyDiMethylSiloxane fiber (Supelco; Bellefonte, PA, USA) for 30 min at 20 °C (Solid Phase Micro Extraction, SPME; Arthur and Pawliszyn, 1990). The analytes adsorbed on the fiber were then desorbed into the GC column headspace at 220 °C (Tassi et al., 2012a, 2015a, 2015b). Carbon dioxide



and H<sub>2</sub>S, dissolved into the alkaline solution of the sampling flasks, were analyzed as CO<sub>3</sub><sup>2-</sup> by automatic titration (AT; Metrohm 794 Basic Titrimo) using a 0.5 M HCl solution, and SO<sub>4</sub><sup>2-</sup> by ionic chromatography (IC; Metrohm 761 Compact) after oxidation with H<sub>2</sub>O<sub>2</sub>, respectively (Montegrossi et al., 2001; Vaselli et al., 2006). Analytical errors for AT, IC and GC were <5%.

The carbon isotopic composition of CO<sub>2</sub> and CH<sub>4</sub> ( $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$ , expressed as ‰ vs. V-PDB) was analyzed by Cavity Ring-Down Spectroscopy (CRDS) using a Picarro G2201-i Analyzer. In order to avoid interferences, the instrument inlet line was equipped with (i) a Drierite trap and (ii) a copper trap to remove water vapor and H<sub>2</sub>S, respectively. According to the operative ranges of the Picarro G2201-i instrument, gas samples showing CO<sub>2</sub> and CH<sub>4</sub> concentrations higher than 2000 ppmv and 500 ppmv, respectively, were diluted with high purity chromatographic air. Gas samples with CO<sub>2</sub>/CH<sub>4</sub> ratios higher than those of the operative ranges were treated by using a bubbler partially filled with a 4 M NaOH solution to remove carbon dioxide prior the CRDS analysis. Internal standards consisting of CO<sub>2</sub> and CH<sub>4</sub> (Air Liquide), with  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$  of -28 and -60‰ vs. V-PDB were used to calibrate and test the reproducibility of the Picarro measurements. The analytical error for  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$  was 0.16 and 1.15‰, respectively, whilst the concentrations of CO<sub>2</sub> and CH<sub>4</sub> were differing of <5% and 10%, respectively, when compared to those measured by GC.

## 4. Results

### 4.1. Solfatara crater

#### 4.1.1. Chemical composition of fumarolic gases

Fumarolic gases were collected from Bocca Grande (SF1) and Bocca Nuova (SF2) vents, located in the eastern portion of the crater (Fig. 1b). The chemical composition of fumarolic dry gases (SF1 and SF2; Table S11; Fig. 1b) was largely dominated by CO<sub>2</sub> (up to 983 mmol/mol), followed by H<sub>2</sub>S (up to 15 mmol/mol), N<sub>2</sub> and H<sub>2</sub> (up to 3.1 and 2.3 mmol/mol, respectively). Minor amounts of CH<sub>4</sub> (up to 66  $\mu\text{mol/mol}$ ) and C<sub>2</sub>H<sub>6</sub> (up to 3.9  $\mu\text{mol/mol}$ , respectively) were also measured. Molecular oxygen (O<sub>2</sub>) and Ar were present at low concentrations ( $\leq 4.1$  and 3.6  $\mu\text{mol/mol}$ , respectively). Benzene (C<sub>6</sub>H<sub>6</sub>), C<sub>3</sub>H<sub>8</sub> and iC<sub>4</sub>H<sub>8</sub> were up to 1.9, 0.81 and 0.75  $\mu\text{mol/mol}$ , respectively.

The isotopic composition of CO<sub>2</sub> at SF1 and SF2 were from -1.3 to -1.1‰, whilst those of CH<sub>4</sub> were from -18.7 and -18.5‰, respectively (Table S11). These values are consistent with those reported from previous studies carried out for the Solfatara fumaroles, i.e.  $\delta^{13}\text{C-CO}_2$  from -2 to -0.95‰ (Chiodini et al., 2008; Tassi et al., 2015a; Vaselli et al., 2011) and  $\delta^{13}\text{C-CH}_4$  from -18.1 to -17.8‰ (Tassi et al., 2012b).

#### 4.1.2. Soil temperatures, diffuse CO<sub>2</sub> fluxes from the soil and chemical composition of interstitial soil gases

Soil temperature and  $\Phi\text{CO}_2$  measurements, and soil gas sampling were carried out at 54 sites (Fig. 1b). Soil temperatures at 20 cm depth ranged from 25.3 to 72.7 °C (Table S11). The highest temperatures were measured in the surroundings of the Fangaia mud pool, in agreement with those reported by other investigations (e.g. Byrdina et al., 2014; Chiodini et al., 2001; Montanaro et al., 2017; Tassi et al., 2013), although relatively high temperatures (up to 53.4 °C) were also recorded on the NW inner flank of the crater. Differently, temperatures in the vegetated portion of the crater and outside the crater were <35 °C.

Diffuse CO<sub>2</sub> fluxes from the soil varied over a wide range, i.e. from 5.0 to 2400 g m<sup>-2</sup> day<sup>-1</sup> (Table S11), the highest values (>200 g m<sup>-2</sup> day<sup>-1</sup>) being generally detected in those areas showing relatively high soil temperatures, whereas lower  $\Phi\text{CO}_2$  values (<50 g m<sup>-2</sup> day<sup>-1</sup>) were measured where Mediterranean maquis shrubland occurred.

The chemical composition of interstitial soil gases collected at 20 cm depth (Table S11) varied from CO<sub>2</sub>-dominated to N<sub>2</sub>-dominated. The former had CO<sub>2</sub>/N<sub>2</sub> ratios ranging from 1.1 to 28 whilst the latter had

CO<sub>2</sub>/N<sub>2</sub> ratios from 0.04 to 0.72. The CO<sub>2</sub>-dominated soil gases, collected from sites with  $\Phi\text{CO}_2$  values ranging from 213 to 2400 g m<sup>-2</sup> day<sup>-1</sup> and temperatures from 31.0 to 72.7 °C, were characterized by CO<sub>2</sub> concentrations between 517 and 965 mmol/mol and relevant concentrations of H<sub>2</sub>S and H<sub>2</sub> (up to 0.94 and 0.81 mmol/mol, respectively). In these samples, the concentrations of CH<sub>4</sub> varied from 1.5 to 29  $\mu\text{mol/mol}$ , whilst those of C<sub>2</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> were up to 3.9 and 2.6  $\mu\text{mol/mol}$ , respectively. Minor amounts of C<sub>3</sub>H<sub>8</sub> and iC<sub>4</sub>H<sub>8</sub> ( $\geq 0.19$  and  $\geq 0.15$   $\mu\text{mol/mol}$ , respectively) were also measured. The concentrations of N<sub>2</sub>, O<sub>2</sub> and Ar were relatively low ( $\leq 480$ ,  $\leq 10$ , and  $\leq 3.3$  mmol/mol, respectively). The N<sub>2</sub>-dominated soil gases, collected from sites with  $\Phi\text{CO}_2$  values ranging from 5 to 440 g m<sup>-2</sup> day<sup>-1</sup> and temperatures from 25.3 to 57.6 °C, showed concentrations of N<sub>2</sub>, O<sub>2</sub>, and Ar up to 923, 99 and 12 mmol/mol, respectively, whilst those of CO<sub>2</sub> were from 33 to 418 mmol/mol. Relatively low contents of H<sub>2</sub>S, H<sub>2</sub> ( $\leq 0.23$  and  $\leq 0.25$  mmol/mol, respectively), C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and iC<sub>4</sub>H<sub>8</sub> ( $\leq 1.3$ ,  $\leq 0.76$ ,  $\leq 0.26$  and  $\leq 0.25$   $\mu\text{mol/mol}$ , respectively) were measured, whilst CH<sub>4</sub> varied over a wide range, i.e. from 1.7 to 55  $\mu\text{mol/mol}$ .

The isotopic composition of CO<sub>2</sub> ranged from -0.76 to 2.28‰ in the CO<sub>2</sub>-dominated gases, whereas a wider range of  $\delta^{13}\text{C-CO}_2$  values were measured in those interstitial gases dominated by N<sub>2</sub>, i.e. from -14.0 to 1.18‰ (Table S11). Differently, the  $\delta^{13}\text{C-CH}_4$  values showed large variations in both CO<sub>2</sub>- and N<sub>2</sub>-dominated gases, since they were ranging from -47.1 to 27.5‰ and from -43.6 to 10.9‰, respectively (Table S11).

### 4.2. Monterotondo M.mo

#### 4.2.1. Chemical composition of fumarolic gases

The field survey focused on a fumarolic and hydrothermally altered area (-0.01 km<sup>2</sup>; Fig. 1c) located in close proximity to the Lagoni geothermal power plant ("Nuova Monterotondo" ENEL Ltd.), inside "Le Biancane" Natural Park, north of Monterotondo M.mo village. The chemical composition of the dry gases from the fumarolic discharges (Fig. 1c; Table S12) was dominated by CO<sub>2</sub> (from 849 to 870 mmol/mol), followed by N<sub>2</sub> (from 107 to 131 mmol/mol), H<sub>2</sub>S (from 7.6 to 8.5 mmol/mol), H<sub>2</sub> (from 7.3 to 8.1 mmol/mol), and CH<sub>4</sub> (from 4200 to 4650  $\mu\text{mol/mol}$ ). Concentrations of O<sub>2</sub> and Ar were  $\leq 1.9$  and  $\leq 0.76$  mmol/mol, respectively. Among VOCs, C<sub>2</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> were the most abundant species (ranging from 6.3 to 7.7  $\mu\text{mol/mol}$  and from 2.7 to 3.2  $\mu\text{mol/mol}$ , respectively), whereas C<sub>3</sub>H<sub>8</sub> and iC<sub>4</sub>H<sub>8</sub> had lower contents ( $\leq 1.6$  and  $\leq 1.9$   $\mu\text{mol/mol}$ , respectively).

The isotopic composition of CO<sub>2</sub> and CH<sub>4</sub> ranged from -3.5 to -3.2‰ and from -27.1 to -25.5‰, respectively (Table S12), in agreement with the  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$  values (from -7.1 to -1.4 and from -31.7 to -20.9‰) reported for hydrothermal fluids from geothermal wells (Gherardi et al., 2005) and fumarolic discharges (Tassi et al., 2012b) in the Larderello geothermal field.

#### 4.2.2. Soil temperatures, diffuse CO<sub>2</sub> fluxes from the soil and chemical composition of interstitial soil gases

Soil temperatures,  $\Phi\text{CO}_2$  measurements and soil gas sampling were carried out in 35 sites (Fig. 1c). Soil temperatures varied from 28.8 to 94.9 °C (Table S12). The highest temperatures were recorded in the northernmost and southernmost edges of the study area. Soil CO<sub>2</sub> fluxes showed a large variability: from 1.2 to 1920 g m<sup>-2</sup> day<sup>-1</sup> (Table S12), and the highest  $\Phi\text{CO}_2$  values were measured in the proximity of the fumarolic emissions (Fig. 1c).

Interstitial soil gases collected at depths ranging from 10 to 20 cm were characterized by CO<sub>2</sub>- or N<sub>2</sub>-dominated compositions (Table S12). The CO<sub>2</sub>-dominated gases were associated with  $\Phi\text{CO}_2$  values ranging from 271 to 1920 g m<sup>-2</sup> day<sup>-1</sup> and temperatures from 47.7 to 94.5 °C, with CO<sub>2</sub> concentrations from 555 to 912 mmol/mol, whilst those of N<sub>2</sub> and Ar were  $\leq 428$  and  $\leq 4.5$  mmol/mol, respectively. Concentrations of O<sub>2</sub> varied over 2 orders of magnitude: from 0.21 to 13 mmol/mol. Hydrogen sulfide and H<sub>2</sub> showed contents ranging from 0.07 to 0.56

mmol/mol and from 0.05 to 0.24 mmol/mol, respectively, whilst those of CH<sub>4</sub> ranged from 2.3 to 355 μmol/mol. Light alkanes, i.e. C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, were characterized by concentrations varying from 1.1 to 5.5 μmol/mol and from 0.21 to 0.95 μmol/mol, respectively, whilst those of C<sub>6</sub>H<sub>6</sub> and iC<sub>4</sub>H<sub>8</sub> ranged from 0.74 to 3.1 μmol/mol and from 0.22 to 1.3 μmol/mol, respectively. The N<sub>2</sub>-dominated gases, collected from sites with ΦCO<sub>2</sub> values ranging from 1.2 to 94 g m<sup>-2</sup> day<sup>-1</sup> and temperatures from 28.8 to 94.9 °C, were characterized by N<sub>2</sub> and CO<sub>2</sub> concentrations ≥773 and ≤215 mmol/mol, respectively. Argon and O<sub>2</sub> contents varied from 8.2 to 14 mmol/mol and from 2.1 to 123 mmol/mol, respectively. Hydrogen sulfide and H<sub>2</sub> were sporadically detected at concentrations ≤0.16 and ≤0.11 mmol/mol, respectively, whilst those of CH<sub>4</sub> varied from 1.50 to 58 μmol/mol. Other VOCs, including C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and iC<sub>4</sub>H<sub>8</sub>, were occasionally detected in few samples at concentrations ≤0.88, ≤0.56, ≤0.21 and ≤0.25 μmol/mol, respectively.

The δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>13</sup>C-CH<sub>4</sub> values in the CO<sub>2</sub>- and N<sub>2</sub>-dominated gases spanned quite largely, i.e. from -16.1 to 3.52‰ and from -43.9 to 21.9‰, respectively (Table SI2).

#### 4.3. Vulcano Island

##### 4.3.1. Chemical composition of fumarolic gases

Carbon dioxide dominated the chemical composition of the dry gases from fumarolic discharges (978 mmol/mol; Table SI3) collected from two vents at Baia di Levante (Fig. 1d), followed by N<sub>2</sub> and H<sub>2</sub>S (from 12 to 13 and from 3.2 to 4.8 mmol/mol, respectively). The fourth most abundant compound was CH<sub>4</sub>, with concentrations ranging from 3.1 to 3.3 mmol/mol, followed by those of H<sub>2</sub> (up to 2.2 mmol/mol), whilst those of Ar and O<sub>2</sub> were up to 0.25 and 0.019 mmol/mol. Among VOCs, C<sub>2</sub>H<sub>6</sub> was the most abundant species, with concentrations up to 6.80 μmol/mol, whilst those of C<sub>3</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>6</sub> and iC<sub>4</sub>H<sub>8</sub> were up to 0.71, 0.43 and 0.11 μmol/mol, respectively.

The δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>13</sup>C-CH<sub>4</sub> values were from -2.3 to -2.1‰ and from -8.1 to -7.5‰ (Table SI3). Similar values were reported for δ<sup>13</sup>C-CO<sub>2</sub> (from -3.1 to -1.7‰) by Capasso et al. (1997) and for δ<sup>13</sup>C-CH<sub>4</sub> (from -7.3 to -5.0‰) by Panichi and Noto (1992) and Nerozzi (2016).

##### 4.3.2. Soil temperatures, diffuse CO<sub>2</sub> fluxes from the soil and chemical composition of interstitial soil gases

Eleven sites were selected at Baia di Levante (Fig. 1d) for temperature and ΦCO<sub>2</sub> measurements and soil gas sampling at 10 cm depth (except for site VI1 where a thick and hard carapace did not allow to reach depths >5 cm) and 30 cm depth (except for sites where the soil gas sampling was impeded by the shallowness of the marine water table). Soil temperatures measured at 5 and 10 cm depths ranged from 21.5 to 37.5 °C, whereas they varied from 27 to 30.9 °C at 30 cm depth (Table SI3). Diffuse CO<sub>2</sub> fluxes ranged from 2.6 to 346 g m<sup>-2</sup> day<sup>-1</sup> (Table SI3). Nitrogen was the most abundant gaseous species of the interstitial soil gases, ranging from 537 to 981 mmol/mol and decreasing with increasing sampling depth (Table SI3). Ar and O<sub>2</sub> concentrations varied from 6.2 to 15 mmol/mol and from 2.9 to 51 mmol/mol, respectively, at shallow depths and from 7.5 to 15 mmol/mol and 3.1 to 29 mmol/mol, respectively, at 30 cm depth. The CO<sub>2</sub> concentrations, inversely correlated to those of N<sub>2</sub>, varied from 3.2 to 411 mmol/mol at shallow depths and showed a direct correlation with the sampling depth, with concentrations at 30 cm depth (from 15 to 216 mmol/mol) from 3.1 to 5.8 times higher than those measured at 10 cm depth at the same sites (Table SI3). Similar trends were shown by the CH<sub>4</sub> concentrations that ranged from 1.7 to 3.9 μmol/mol at 5 and 10 cm depths and from 4.2 to 7.5 μmol/mol at 30 cm depth. Hydrogen sulfide (≤0.58 mmol/mol), H<sub>2</sub> (≤0.44 mmol/mol), C<sub>2</sub>H<sub>6</sub> (≤0.84 μmol/mol), C<sub>6</sub>H<sub>6</sub> (≤0.23 μmol/mol) and C<sub>3</sub>H<sub>8</sub> (≤0.22 μmol/mol) were sporadically detected.

The δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>13</sup>C-CH<sub>4</sub> values ranged from -15.5 to 1.44‰ and from -47.7 to 6.47‰, respectively, with no clear trend with respect to sampling depth (Table SI3).

## 5. Discussion

Carbon dioxide was the dominant gas species in the investigated hydrothermal fluids. Accordingly, the uprising of CO<sub>2</sub>-rich fluids from the deep hydrothermal systems produced anomalous ΦCO<sub>2</sub> values in the investigated areas, i.e. up to 2400 g m<sup>-2</sup> day<sup>-1</sup>, 1920 g m<sup>-2</sup> day<sup>-1</sup> and 346 g m<sup>-2</sup> day<sup>-1</sup> at Solfatara crater, Monterotondo M.mo and Vulcano Island, respectively. High ΦCO<sub>2</sub> values were generally associated with (i) high soil temperatures (Fig. 2a), produced by steam condensation at relatively shallow depths, and (ii) high concentrations of CO<sub>2</sub> in interstitial soil gases (Fig. 2b), coupled with relevant concentrations of other hydrothermal-derived gases (H<sub>2</sub>S, H<sub>2</sub> and VOCs) and inversely correlated to air-related species (N<sub>2</sub>, O<sub>2</sub> and Ar; Fig. 2c).

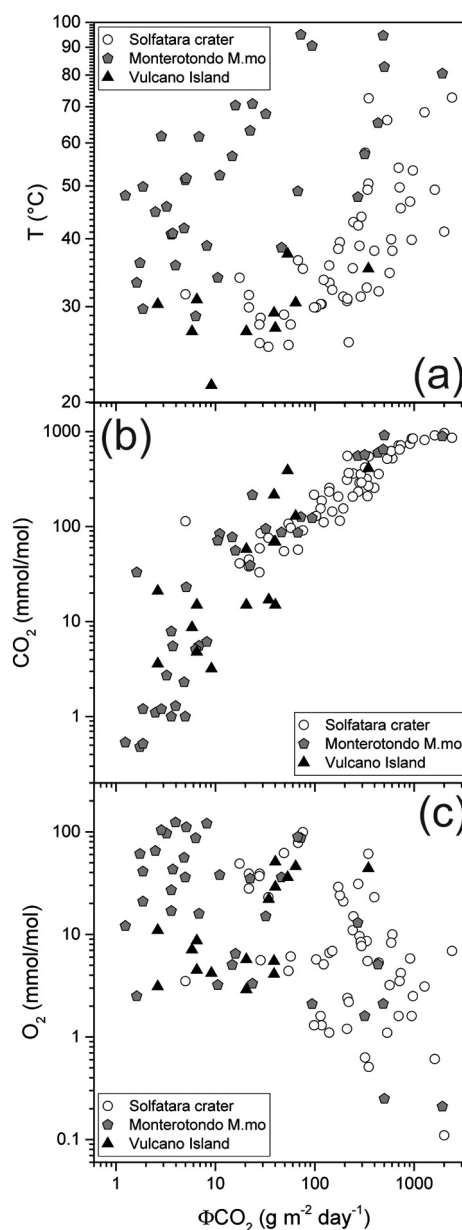


Fig. 2. (a) Soil temperature, (b) soil CO<sub>2</sub> content and (c) soil O<sub>2</sub> concentration vs. ΦCO<sub>2</sub> binary diagrams for interstitial soil gases from Solfatara crater (white circles), Monterotondo M.mo (grey pentagons) and Vulcano Island (black triangles).

The isotopic composition of CO<sub>2</sub> from the interstitial soil gases approached the δ<sup>13</sup>C-CO<sub>2</sub> values of the fumarolic discharges at increasing CO<sub>2</sub> concentrations (Fig. 3) and ΦCO<sub>2</sub> values. On the other hand, soil gases with relatively low CO<sub>2</sub> contents, collected from sites characterized by ΦCO<sub>2</sub> values approaching typical background soil CO<sub>2</sub> effluxes fed by biogenic sources in the soil (<50 g m<sup>-2</sup> day<sup>-1</sup>; e.g. Chiodini et al., 2008 and references therein), displayed significantly negative δ<sup>13</sup>C-CO<sub>2</sub> values, pointing to an end-member characterized by isotopically light CO<sub>2</sub>. The latter can be identified with a biogenic component, related to soil respiration, characterized by δ<sup>13</sup>C-CO<sub>2</sub> values ≤ -20‰ (Cheng, 1996; Chiodini et al., 2008; Degens, 1969; Viveiros et al., 2010). As evidenced in Fig. 3, the distribution of the measured data is approximately consistent with the theoretical mixing trend between hydrothermal and biogenic CO<sub>2</sub>, coherently with the compositional features of interstitial soil gases.

Nevertheless, the mixing process between hydrothermal and biogenic components does not exhaustively explain the distribution of the measured data, since δ<sup>13</sup>C-CO<sub>2</sub> values higher than those reported for the deep end-member were recorded in all the study areas (Fig. 3). This was clearly evidenced at Solfatara crater (Fig. 3a), where soil gases, characterized by intermediate ΦCO<sub>2</sub> values (up to 972 g m<sup>-2</sup> day<sup>-1</sup>) and CO<sub>2</sub> contents up to 845 mmol/mol, displayed δ<sup>13</sup>C-CO<sub>2</sub> values up to 2.28‰, i.e. significantly heavier than the carbon isotopic values measured at the fumarolic gas discharges.

Different hypotheses can be invoked to explain the observed anomalously high δ<sup>13</sup>C-CO<sub>2</sub> values, as follows: (i) isotope fractionation related to gas diffusion, (ii) partial dissolution of CO<sub>2</sub> in steam condensate, (iii) microbial consumption at shallow depths.

Whilst the upward motion of hydrothermally-derived CO<sub>2</sub> is mainly driven by pressure and temperature gradients (advection) within the CO<sub>2</sub>-enriched soil layer, the gas migration in the shallowest CO<sub>2</sub>-depleted portions of the soil is mainly controlled by diffusion, i.e. a transport mechanism controlled by concentration gradients. Advection is expected to produce negligible isotopic fractionation (e.g. Etiope et al., 2009 and references therein; Kayler et al., 2010), and accordingly, CO<sub>2</sub>-rich soil gases from sites with ΦCO<sub>2</sub> values ≥ 1275 g m<sup>-2</sup> day<sup>-1</sup> at Solfatara crater displayed δ<sup>13</sup>C-CO<sub>2</sub> values similar to those recorded in the fumarolic gas discharges (Fig. 3a). Conversely, diffusion through the soil is able to induce a fractionation effect due to the faster kinetics of <sup>12</sup>CO<sub>2</sub> escaping towards the atmosphere, producing an increase of δ<sup>13</sup>C-CO<sub>2</sub> values within the shallow CO<sub>2</sub>-depleted soil layers (e.g. Cerling and

Quade, 1993; Capasso et al., 1997, 2001b; Di Martino et al., 2016; Etiope et al., 2009 and references therein; Federico et al., 2010; Kayler et al., 2010). Nevertheless, even though it was not possible to develop a diffusion-enrichment model to be compared with field data due to the lack of δ<sup>13</sup>C-CO<sub>2</sub> measurements systematically performed along vertical profiles within the soil, the hypothesis of a <sup>13</sup>C enrichment induced by gas diffusion does not agree with the high ΦCO<sub>2</sub> values (up to 972 g m<sup>-2</sup> day<sup>-1</sup>) and CO<sub>2</sub> contents (>800 mmol/mol) characterizing soil gases, whose δ<sup>13</sup>C-CO<sub>2</sub> values were up to 3‰ higher than those measured in fumarolic discharges.

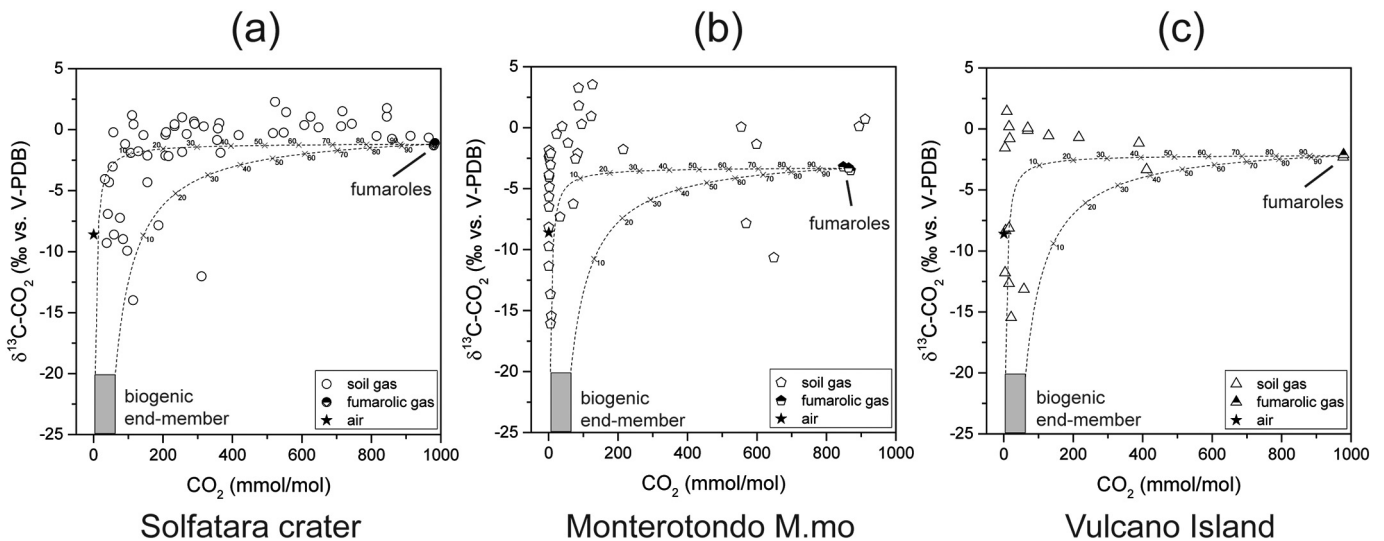
Steam condensation related to hydrothermal fluids upward motion largely occurs at Solfatara crater, producing a water-saturated layer that emerges from the Fangaia mud pool (Chiodini et al., 2001; Bruno et al., 2007; De Landro et al., 2017; Gresse et al., 2017). The isotope fractionation effect related to the dissolution of gaseous CO<sub>2</sub> into the aqueous solution is expected to produce a relative enrichment in <sup>13</sup>C in the residual gas, according to the isotopic enrichment factor ε<sub>CO<sub>2</sub>(aq)-CO<sub>2</sub>(g)</sub> defined by Deines et al. (1974), as follows:

$$\varepsilon_{\text{CO}_2(\text{aq})-\text{CO}_2(\text{g})} = \frac{6300}{T^2} - 0.91 \quad (2)$$

where T is the temperature in K. Isotope fractionation related to partial dissolution of CO<sub>2</sub> into steam condensate was indeed previously invoked to explain δ<sup>13</sup>C values recorded in soil gas CO<sub>2</sub> from Iwojima volcano (Japan), which were up to ~6‰ higher than those in fumarolic fluids (Notsu et al., 2005). The partial dissolution of deep-sourced CO<sub>2</sub> into the steam condensate at relatively shallow depths can be modeled as a Rayleigh-type fractionation process under open-system conditions, as follows:

$$\delta^{13}\text{C}-\text{CO}_{2,\text{res}} = \left[ \left( \delta^{13}\text{C}-\text{CO}_{2,\text{ini}} + 1000 \right) \times f^{\left( \frac{\varepsilon_{\text{CO}_2(\text{aq})-\text{CO}_2(\text{g})}}{1000} \right)} \right] - 1000 \quad (3)$$

where δ<sup>13</sup>C-CO<sub>2,ini</sub> is the isotopic composition of CO<sub>2</sub> in the uprising hydrothermal fluids (assumed as equal to the average value measured in fumarolic gases), whilst f and δ<sup>13</sup>C-CO<sub>2,res</sub> are the fraction and isotopic composition of the residual CO<sub>2</sub> after the interaction with condensates, respectively. Accordingly, an enrichment of 3‰ of δ<sup>13</sup>C-CO<sub>2</sub> values in soil gases would require a dissolution of ~95% of the deep-sourced CO<sub>2</sub>. However, such an intense CO<sub>2</sub> scrubbing is compatible neither



**Fig. 3.** δ<sup>13</sup>C-CO<sub>2</sub> vs. CO<sub>2</sub> binary diagrams for interstitial soil gases from (a) Solfatara crater, (b) Monterotondo M.mo and (c) Vulcano Island. Fumarolic discharges (black and white symbols) and air (black star; Keeling et al., 2005) are reported. The mixing lines between (i) a hydrothermal component, with CO<sub>2</sub> and δ<sup>13</sup>C-CO<sub>2</sub> corresponding to the average values measured in fumarolic gases from each study area, and (ii) a biogenic component, with CO<sub>2</sub> concentrations from 5 to 50 mmol/mol and δ<sup>13</sup>C-CO<sub>2</sub> values ranging from -25 to -20‰, are shown. The fraction (in percentage) of the hydrothermal component involved in the mixture is reported.



with the acidic conditions of the steam condensate (pH values at Fangaia mud pool were  $\leq 1.8$ ; Crognale et al., 2018; Rouwet et al., 2018) nor with the high  $\Phi\text{CO}_2$  values measured at sites displaying  $^{13}\text{C}$  enriched soil gases.

Accordingly, biological  $\text{CO}_2$  uptake and fixation processes, which are expected to produce a  $^{13}\text{C}$ -rich residual  $\text{CO}_2$  in interstitial soil gases (e.g. Freude and Blaser, 2016 and references therein; Tassi et al., 2015b and references therein), are the most likely responsible for the heavier  $\delta^{13}\text{C}\text{-CO}_2$  values. Accordingly, autotrophic bacteria were isolated from terrestrial solfataric fields (e.g. Huber et al., 2000; Stetter, 1999), including Solfatara crater (Crognale et al., 2018), where the occurrence of autotrophic  $\text{CO}_2$  fixation in hydrothermal deposits was also confirmed based on the  $\delta^{13}\text{C}$  value of organic carbon (Glamočlija et al., 2004).

In fact, most extremophiles adapted to live in solfataric fields exhibit a chemolithoautotrophic metabolism (Stetter, 2006). Chemosynthetic microbes gain energy for the conversion of  $\text{CO}_2$  or other carbon-containing molecules into organic matter from the oxidation of inorganic compounds, such as  $\text{H}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$  (e.g. Carere et al., 2017; Mohammadi et al., 2017), which are largely supplied by the uprising hydrothermal fluids. Accordingly, soil gases from the investigated areas were generally characterized by  $\text{CO}_2/\text{H}_2$ ,  $\text{CO}_2/\text{H}_2\text{S}$  and  $\text{CO}_2/\text{CH}_4$  ratios largely higher than those measured in fumarolic fluids, suggesting the involvement of the deep-sourced reduced gaseous compounds in shallow oxidation processes.

Differently from  $\text{CO}_2$ , the  $\text{CH}_4$  concentrations in fumarolic gases showed large differences among the study areas ( $\sim 65$   $\mu\text{mol/mol}$  at Solfatara crater;  $\sim 4450$   $\mu\text{mol/mol}$  at Monterotondo M.mo;  $\sim 3200$   $\mu\text{mol/mol}$  at Vulcano Island), likely related to the different temperature and redox conditions characterizing the three hydrothermal systems. The  $\text{CH}_4$  concentrations from soil gases were up to 55, 355 and 7.5  $\mu\text{mol/mol}$  at Solfatara crater, Monterotondo M.mo and Vulcano Island, respectively, and inversely correlated to  $\text{O}_2$  (Fig. 4), suggesting that aerobic conditions may limit the  $\text{CH}_4$  levels within the soil pores. On the other hand, differently from other VOCs, especially  $\text{C}_6\text{H}_6$ ,  $\text{iC}_4\text{H}_8$  and even short-chain  $\text{C}_{2-3}$  alkanes, which were strictly correlated to the hydrothermal fluid supply, no evident correlation between  $\text{CH}_4$  and  $\text{CO}_2$  was observed, suggesting that these gas species undergo different processes during fluids uprising towards the surface. In particular, interstitial soil gases were mostly characterized by  $\text{CO}_2/\text{CH}_4$  ratios higher than those recorded in fumarolic fluids, evidencing that methanotrophy is able to significantly affect  $\text{CH}_4$  in the soil.

Wide variations in the isotopic composition of  $\text{CH}_4$  in interstitial soil gases were observed, since  $\delta^{13}\text{C}\text{-CH}_4$  values ranging from  $-47.1$  to  $27.5\%$  at Solfatara crater, from  $-43.9$  to  $21.9\%$  at Monterotondo M.

mo, from  $-47.7$  to  $6.47\%$  at Vulcano Island were registered. These values significantly differ with respect to those of the fumarolic gases for which a narrower range was observed: from  $-18.7$  to  $-18.5\%$  at Solfatara crater; from  $-27.1$  to  $-25.5\%$  at Monterotondo M.mo; from  $-8.1$  to  $-7.5\%$  at Vulcano Island.

In Fig. 5, the  $\delta^{13}\text{C}\text{-CH}_4$  values from the interstitial soil gases are plotted vs. the  $\text{CH}_4$  contents for Solfatara (Fig. 5a), Monterotondo M.mo (Fig. 5b) and Vulcano Island (Fig. 5c), together with the curves of mixing of the deep hydrothermal end-member (i.e. average fumarolic  $\text{CH}_4$  and  $\delta^{13}\text{C}\text{-CH}_4$  values) with (i) air (“mixing 1”), characterized by  $\text{CH}_4$  and  $\delta^{13}\text{C}\text{-CH}_4$  values of  $\sim 1.8$   $\mu\text{mol/mol}$  and  $\sim -47\%$ , respectively (Nisbet et al., 2016 and references therein), and (ii) a shallow biogenic end-member (“mixing 2”). The latter was assumed to be represented by the soil gas from each study area characterized by (i)  $\delta^{13}\text{C}\text{-CH}_4$  values approaching those of typical microbial  $\text{CH}_4$ , i.e.  $\leq -50\%$  (e.g. McCollom and Seewald, 2007; Schoell, 1980; Whiticar, 1999) and (ii) isotopically light  $\text{CO}_2$ . As shown in Fig. 5, the distribution of most values does not follow the depicted mixing trends. Accordingly, secondary processes occurring during hydrothermal fluids upward motion in diffuse degassing areas largely control the isotopic composition of  $\text{CH}_4$ . Despite the clear contribution from hydrothermal fluids revealed by  $\delta^{13}\text{C}\text{-CO}_2$  values within the fumarolic range and relatively high soil  $\text{CO}_2$  fluxes,  $\text{CH}_4$ -rich soil gases with low  $\delta^{13}\text{C}\text{-CH}_4$  values ( $\sim -40\%$ ) were observed at both Solfatara crater and Monterotondo M.mo (Fig. 5a, b). These soil gases were characterized by a difference between  $\delta^{13}\text{C}\text{-CO}_2$  and  $\delta^{13}\text{C}\text{-CH}_4$  values of  $\sim 35\%$  (Tables S11, S12), similar to the carbon isotopic fractionation values obtained by Valentine et al. (2004) during experimental studies on  $\text{H}_2/\text{CO}_2$  methanogenesis. Accordingly, methanogenic activity may partially contribute to the production of  $\text{CH}_4$  under the reducing conditions characterizing the deeper soil layers. On the other hand, the markedly high  $\delta^{13}\text{C}\text{-CH}_4$  values characterizing soil gases with relatively low  $\text{CH}_4$  contents could be related to the occurrence of  $\text{CH}_4$  consumption driven by microbial activity at shallow depths (methanotrophy). In fact,  $^{12}\text{CH}_4$  tends to be oxidized faster than  $^{13}\text{CH}_4$  by methanotrophs, favoring the formation of  $^{13}\text{C}$ -rich residual methane (e.g. Whiticar, 1999).

The isotope fractionation effect related to methanotrophy was depicted on Fig. 5 considering a Rayleigh-type fractionation process, as follows:

$$\delta^{13}\text{C}\text{-CH}_{4\_res} = \left[ (\delta^{13}\text{C}\text{-CH}_{4\_ini} + 1000) \times f^{\left(\frac{1}{\alpha_{\text{CH}_4\text{-CH}_3\text{OH}}}\right)} \right] - 1000 \quad (4)$$

where  $\delta^{13}\text{C}\text{-CH}_{4\_ini}$  is the isotopic composition of  $\text{CH}_4$  in the uprising hydrothermal fluids (assumed as equal to the average value measured in fumarolic gases or, alternatively, to the  $\delta^{13}\text{C}\text{-CH}_4$  value of  $\text{CH}_4$ -rich soil gases likely related to methanogenesis),  $\delta^{13}\text{C}\text{-CH}_{4\_res}$  is the isotopic composition of the residual  $\text{CH}_4$  after the microbial uptake,  $f$  is the fraction of residual  $\text{CH}_4$  and  $\alpha_{\text{CH}_4\text{-CH}_3\text{OH}}$  is the carbon isotope fractionation factor for aerobic bacterial first oxidation of  $\text{CH}_4$  ranging from 1.005 to 1.035 (Templeton et al., 2006). The resulting curves agreed relatively well with the measured data (Fig. 5), suggesting that methanotrophic activity in the soil can partially reduce the emissions of deep-sourced (either thermogenic or biogenic)  $\text{CH}_4$  from solfataric fields. The widest shifts in  $\delta^{13}\text{C}\text{-CH}_4$  values of soil gases relative to fumarolic discharges ( $\sim 46\%$ ) were observed at Solfatara crater and Monterotondo M.mo (Fig. 5a, b), in sites (S49 and M33) characterized by temperatures and  $\text{O}_2$  contents of  $72$   $^\circ\text{C}$  and  $6.9$   $\text{mmol/mol}$  and  $49$   $^\circ\text{C}$  and  $89$   $\text{mmol/mol}$ , respectively. During methanotrophy, the oxidation of  $\text{CH}_4$  results in a decrease of  $\text{CH}_4$  concentrations, an increase of  $\text{CO}_2$  contents and a shift of  $\delta^{13}\text{C}$  of residual  $\text{CH}_4$  towards heavier values. Accordingly, a progressive increase in the measured  $\delta^{13}\text{C}\text{-CH}_4$  values was associated with increasing  $\text{CO}_2/\text{CH}_4$  ratios in the interstitial soil gases (Fig. 6a), further supporting the hypothesis of  $\text{CH}_4$  consumption in the soil. As evidenced in Fig. 6b, the isotopic shift of  $\delta^{13}\text{C}\text{-CH}_4$  towards positive values was also

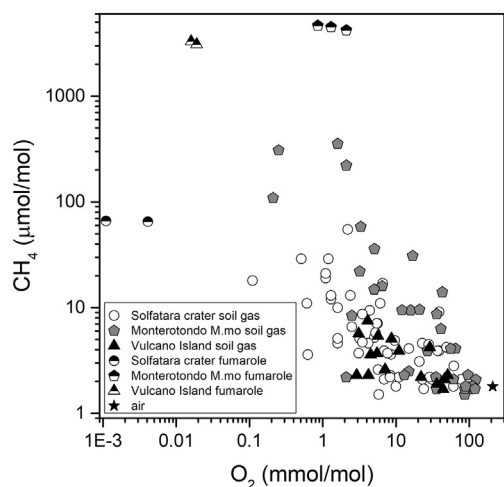
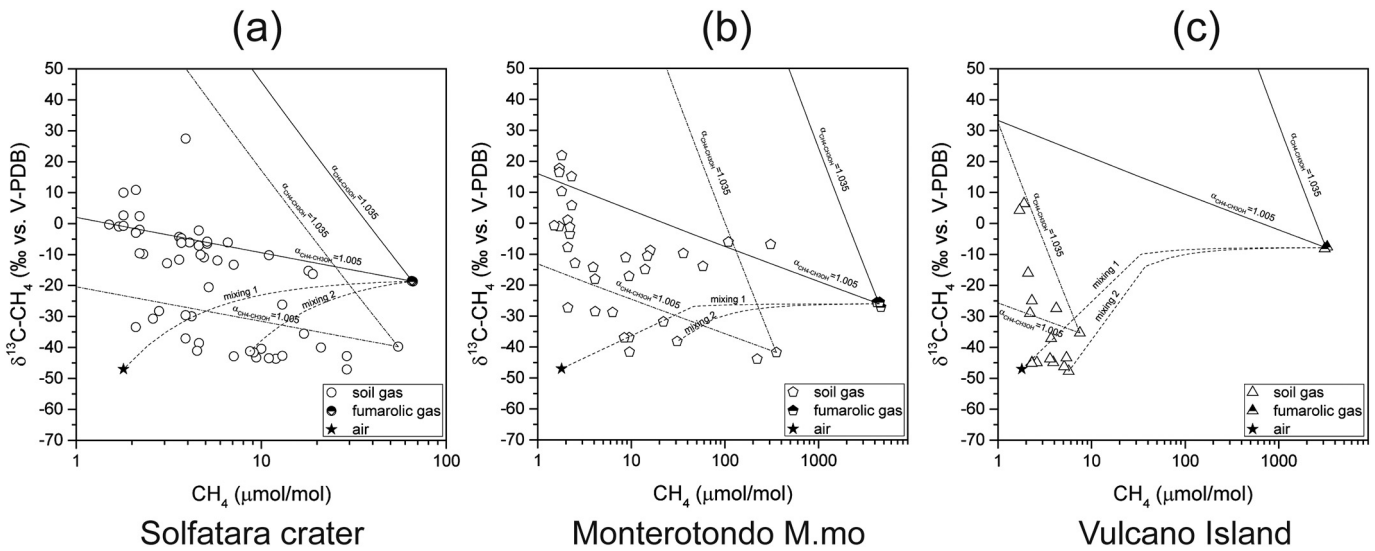


Fig. 4.  $\text{CH}_4$  vs.  $\text{O}_2$  binary diagrams for interstitial soil gases and fumarolic gases (black and white symbols) from (a) Solfatara crater, (b) Monterotondo M.mo and (c) Vulcano Island. The composition of air (black star) is also reported.





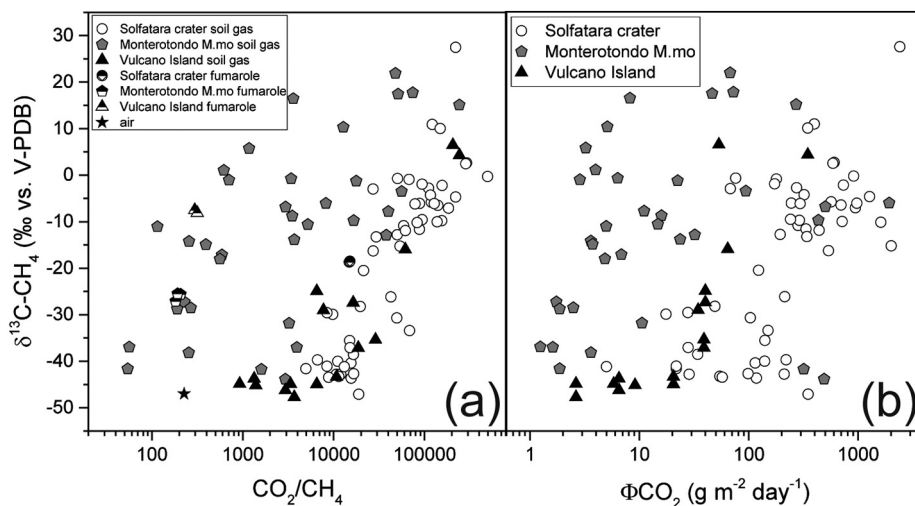
**Fig. 5.**  $\delta^{13}\text{C}\text{-CH}_4$  vs.  $\text{CH}_4$  binary diagrams for interstitial soil gases from (a) Solfatara crater, (b) Monterotondo M.mo and (c) Vulcano Island. Fumarolic gases (black and white symbols) and air (black star) are reported together with mixing lines and Rayleigh fractionation evolution curves, as described in the text.

recorded in interstitial soil gases from sites characterized by relatively high  $\Phi\text{CO}_2$  values, particularly at Solfatara crater (Fig. 6b), where the most positive  $\delta^{13}\text{C}\text{-CH}_4$  value (27.5‰), associated with a  $\text{CO}_2/\text{CH}_4$  ratio ~15 times higher than that measured in fumarolic emissions, was recorded in one soil gas collected from a site characterized by a  $\text{CO}_2$  flux of  $2400\text{ g m}^{-2}\text{ day}^{-1}$ . This evidence suggests that, differently to what observed by Tassi et al. (2013) on the basis of  $\Phi\text{CO}_2$  and  $\Phi\text{CH}_4$  measurements at Solfatara crater, methanotrophy is potentially able to mitigate  $\text{CH}_4$  emissions from hydrothermalized areas also under high diffuse soil flux conditions. If confirmed by further analysis, this scenario would open interesting perspectives in terms of quantification of the impact of natural greenhouse gas sources and development of effective strategies for the abatement of anthropogenic emissions.

**6. Conclusions**

Diffuse degassing from volcanic-hydrothermal areas largely contributes to the emission of greenhouse gases released to the atmosphere, as shown by the soil fluxes of  $\text{CO}_2$  measured in this study at Solfatara crater

(up to  $2400\text{ g m}^{-2}\text{ day}^{-1}$ ), Monterotondo M.mo ( $1920\text{ g m}^{-2}\text{ day}^{-1}$ ) and Baia di Levante at Vulcano Island (up to  $346\text{ g m}^{-2}\text{ day}^{-1}$ ). The chemical and isotopic compositions of interstitial soil gases from these areas also suggested that secondary processes occurring during fluids uprising towards the surface largely affected  $\text{CO}_2$  and  $\text{CH}_4$ . In particular, interstitial soil gases showed a large variability in terms of  $\delta^{13}\text{C}\text{-CH}_4$  due to the presence of significant microbial  $\text{CH}_4$  consumption, even in presence of high soil  $\text{CO}_2$  fluxes and relatively low  $\text{O}_2$ . Methanotrophic activity is apparently characterizing all the investigated areas, though at different extent, as a function of  $\text{CH}_4$  availability in deep sourced gases. This implies that methanotrophy has to be considered a common process in diffuse degassing areas. The comparison between  $\text{CO}_2/\text{CH}_4$  ratios from soil gases and fumarolic discharges suggests that microbial activity in the soil likely contributes to regulate the emission of  $\text{CH}_4$  and, though to a lesser extent, that of  $\text{CO}_2$  from natural environments. Therefore, microbial communities inhabiting soil in hydrothermal diffuse degassing areas play a key role in mitigating climate change by reducing geogenic greenhouse gas emissions (e.g. Gupta et al., 2014; Singh et al., 2010).



**Fig. 6.**  $\delta^{13}\text{C}\text{-CH}_4$  vs. (a)  $\text{CO}_2/\text{CH}_4$  ratios and (b)  $\Phi\text{CO}_2$  binary diagrams for interstitial soil gases from Solfatara crater, Monterotondo M.mo and Vulcano Island. In (a) fumarolic gases (black and white symbols) and air (black star) are also reported.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.11.293>.

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