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Fractionation processes affecting the stable carbon isotope signature of thermal waters from hydrothermal/volcanic systems: The examples of Campi Flegrei and Vulcano Island (southern Italy)

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Abstract

The carbon isotopic composition of dissolved C-bearing species is a powerful tool to discriminate the origin of carbon in thermal waters from volcanic and hydrothermal systems. However, the $\delta^{13}\text{C}$ values of dissolved CO_2 and TDIC (Total Dissolved Inorganic Carbon) are often different with respect to the isotopic signature that characterizes the potential carbon primary sources, i.e. deep hydrothermal reservoirs, magmatic gases and organic activity. The most commonly invoked explanation for such isotopic values is related to mixing processes between deep and shallow end-members. Nevertheless, experimental and empirical investigations demonstrated that isotopic fractionation due to secondary processes acting on the uprising fluids from the hydrothermal reservoirs is able to reproduce the measured isotopic values. In this paper, we investigated the chemistry of thermal waters, collected at Campi Flegrei and Vulcano Island (southern Italy), whose origin is related to interaction processes among magmatic gases, meteoric water, seawater and hosting rocks. A special focus was dedicated to the $\delta^{13}\text{C}$ values of dissolved CO_2 ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$) and total dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{TDIC}}$). The $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values in the water samples from both these systems ranged from (i) those measured in fumarolic gases, likely directly related to the deep hydrothermal-magmatic reservoir, and (ii) those typically characterizing biogenic CO_2 , i.e. produced by microbially-driven degradation of organic matter. A simple mixing model of the two end-members, apparently explaining these intermediate carbon isotopic values, contrasts with the chemical composition of the dissolved gases. On the contrary, isotopic fractionation due to secondary processes, such as calcite precipitation, affecting hydrothermal fluids during their underground circulation, seems to exhaustively justify both the chemical and isotopic data. If not recognized, these processes, which frequently occur in volcanic and hydrothermal systems, may lead to an erroneous interpretation of the carbon source, causing an underestimation of the contribution of the hydrothermal/magmatic fluids to the dissolved carbon species. These results

pose extreme caution in the interpretation of intermediate $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values for the assessment of the carbon budget of hydrothermal-volcanic systems.

Keywords: *thermal waters; carbon isotopes; dissolved CO_2 ; TDIC; volcanic-hydrothermal systems; secondary fractionation processes*

1. Introduction

Fluids from volcanic and hydrothermal systems significantly contribute to the global carbon cycle, since they discharge huge amounts of CO_2 to the atmosphere through active vents (open conduit craters and fumaroles) and diffuse soil degassing (e.g. Chiodini et al., 1998; Aiuppa et al., 2013; Burton et al., 2013; Conde et al., 2014). A significant portion of volcanic/hydrothermal CO_2 dissolves into subsurface waters as HCO_3^- and CO_3^{2-} , as a function of pH, and is discharged from springs and/or shallow wells (e.g. D'Alessandro et al., 1997; Inguaggiato et al., 2005; Chiodini et al., 2015a). The isotopic signature ($\delta^{13}\text{C}$) of dissolved CO_2 and total dissolved inorganic carbon (TDIC) are useful tools to discriminate the different sources of carbon in thermal waters, when a gas-free phase does not occur (e.g. Chiodini et al., 2000, 2004). Distinct $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values can indeed be recognized in C-bearing dissolved species that derive from CO_2 generated by different processes, such as: 1) mantle/magmatic degassing, producing CO_2 typically showing $\delta^{13}\text{C}$ values around -6 ‰ vs. V-PDB (Rollinson, 1993; Sano and Marty, 1995; Hoefs, 2009), i.e. similar to the isotopic value of atmospheric CO_2 (ca. -8 ‰ vs. V-PDB; Scripps CO_2 Program); 2) degradation of organic matter, characterized by CO_2 with $\delta^{13}\text{C} < -20$ ‰ vs. V-PDB (Degens, 1969; Rollinson, 1993; Sano and Marty, 1995); 3) thermometamorphic reactions on carbonate rocks, producing isotopically heavy CO_2 ($\delta^{13}\text{C} = 0 \pm 5$ ‰ vs. V-PDB; Sano and Marty, 1995; Clark, 2015). Despite the isotopic fractionation of CO_2 to form $\text{CO}_{2(\text{aq})}$ and (bi)carbonates species (e.g. Bottinga, 1968; Deines et al., 1974; Mook et al., 1974), this widely accepted classification is not

consistent with the isotopic signature of a number of thermal waters from volcanic and hydrothermal areas, which show $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values ranging from -18‰ to -9‰ vs. V-PDB (e.g. D'Alessandro et al., 1997; Caliro et al., 1999; Federico et al., 2002; Taran et al., 2002; Inguaggiato et al., 2005; Grassa et al., 2006; Yamada et al., 2011; Ruzié et al., 2013; Marrero-Diaz et al., 2015; Morikawa et al., 2016). In most cases, these isotopic values, which are intermediate with respect to those related to mantle/magmatic and biogenic CO_2 , were interpreted as due to mixing processes between deep and shallow/marginal end-members (e.g. Italiano et al., 2009; Fourré et al., 2011; Ruzié et al., 2013). However, other studies demonstrated the strong influence of isotopic fractionation on the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values, which were related to multi-step CO_2 dissolution (e.g. Weinlich, 2005; Gilfillan et al., 2009; Güleç and Hilton, 2016) and carbonate precipitation/dissolution (e.g. Ohwada et al., 2007; Gilfillan et al., 2009; Barry et al., 2014; Güleç and Hilton, 2016). These secondary chemical processes are considered to commonly affect thermal fluids from volcanic and hydrothermal areas (Simmons and Christenson, 1994 and references therein). Hence, they may represent a valuable alternative explanation for $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values not consistent with the primary CO_2 sources.

In the present study, we report a complete dataset, consisting of major ion chemistry, chemical composition of dissolved gases and carbon isotopes ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$), measured in thermal waters from two volcanic systems in Italy: Campi Flegrei (Naples, southern Italy) and Vulcano Island (Aeolian Archipelago, southern Italy) (e.g. Boschetti et al., 2003 and references therein; Valentino and Stanzione, 2003 and references therein). The main aim is to investigate the mechanisms controlling the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values in these fluids, in order to provide insights into the role played by the secondary chemical processes that may affect the estimation of hydrothermal/magmatic CO_2 contribution to the global carbon budget.

2. Geological features and hydrothermal/magmatic systems of the study areas

2.1. Campi Flegrei

The Campi Flegrei caldera (Fig. 1a) is an active volcanic complex occupying $\sim 100 \text{ km}^2$ of the Campanian Plain, NW of Naples (southern Italy). The caldera structure formed during two large eruptions, which produced (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 volcanic system developed within the Campanian graben, where volcanic deposits (K-basalts, trachybasalts, latites, trachytes, alkali-trachytes and phonolites), marine and continental sediments overlie the Mesozoic carbonate basement located at 4 km depth. The last historical eruptive event occurred in 1538 AD (Di Vito et al., 1987), which originated the monogenic tuff cone of Monte Nuovo (Fig. 1a), after about 3,000 years of quiescence.

The hydrothermal system of the Campi Flegrei caldera, which is related to fluids released from a magma chamber located at about 5 km below the town of Pozzuoli (e.g. Gottsmann et al., 2006), is responsible for frequent episodes of ground uplift and subsidence (*bradyseism*) accompanied by seismic activity (e.g. Bonafede and Mazzanti, 1998; Chiodini et al., 2003, 2012, 2015b; Gottsmann et al., 2006).

Two distinct hydrothermal reservoirs, located within the volcanic cover, were recognized in the area: (i) a seawater-contaminated shallow reservoir (depth $< 2 \text{ km}$) diluted by meteoric waters, and (ii) a deep hydrothermal reservoir ($> 2 \text{ km}$) of hypersaline waters (Caprarelli et al., 1997; Valentino and Stanzione, 2003). The surficial expression of the hydrothermal activity within the caldera mostly consists of submarine and inland fumarolic vents, anomalous diffuse soil degassing (e.g. Chiodini et al., 2001; Todesco et al., 2003; Caliro et al., 2007; Vaselli et al., 2011; Passaro et al., 2016), and thermal water discharges and wells (e.g. Valentino and Stanzione, 2003, 2004).

2.2. Vulcano Island

Vulcano Island is the southernmost island of the Aeolian Archipelago (southern Italy), a subduction-related volcanic arc in the Southern Tyrrhenian Sea (Fig. 1b). It consists of a main

edifice, mostly developed during the Pleistocene and Holocene through several stages of stratocone building and caldera collapse (Keller, 1980; De Astis et al., 1997), and a smaller island (Vulcanello), made of lavas and pyroclastic cones formed by nearly continuous activity between 1000 and 1250 AD (Arrighi et al., 2006). The last eruptive event occurred in 1888-1890 (Clocchiatti et al., 1994) from La Fossa, a 391 m high cone (Fig. 1b) having a base diameter of 1 km. La Fossa summit crater is currently characterized by intense fumarolic activity, mostly occurring in its NW sector. The fumaroles are characterized by outlet temperatures up to 450 °C and a typical magmatic composition, with a dry gas fraction dominated by CO₂ and relatively high concentrations of HCl, SO₂, H₂S and HF (e.g. Capasso et al., 1997, 1999; Inguaggiato et al., 2012). Subaereal and submerged fumaroles, with outlet temperatures < 100 °C, occur at Baia di Levante, the bay delimiting the eastern side of a flat isthmus that connects Vulcano to Vulcanello (Fig. 1b). These fluid discharges, which show relatively high CH₄ and H₂S contents and the virtual absence of high-temperature magmatic gases (SO₂, HCl and HF), are fed by a shallow hydrothermal source heated by the uprising hot magmatic fluids (Capaccioni et al., 2001). According to the geochemical measurements carried out on fluids from a geothermal well drilled in the 1950's near the Baia di Levante beach (Sommaruga, 1984), the hydrothermal system consists of multilevel water bodies, as follows: (i) a shallow aquifer (at 7-14 m depth) at ~100 °C, (ii) an intermediate aquifer (at 90-95 m depth) having a temperature of ~136 °C, and (iii) a deep aquifer (at 185-236 m depth) at ~200 °C, the latter showing a seawater-like chemical composition. Strong soil degassing affects both the surroundings of the volcanic edifice and some portions of the Vulcano Porto plain located NW of La Fossa cone (Carapezza et al., 2011; Inguaggiato et al., 2012), where several domestic thermal wells were drilled.

3. Materials and methods

3.1. Water and dissolved gas sampling

Water and dissolved gas samples were collected during three field campaigns in 2013 and 2015 from (i) 17 wells and the bottom of Lake Averno (33 m depth) in the Campi Flegrei caldera (Fig. 1a), and (ii) 20 wells located within the area of Vulcano Porto village at Vulcano Island (Fig. 1b).

Three water aliquots were collected at each sampling site, as follows: (1) one aliquot in a 125 mL polyethylene bottle, for the determination of main anions, (2) one filtered (0.45 μm) aliquot in a 50 mL polyethylene bottle containing 0.5 mL of 30 % Suprapur HCl, for the analysis of main cations, and (3) a third aliquot, sampled in evacuated glass vials containing 2 mL of anhydrous phosphoric acid, for isotope analyses of total dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{TDIC}}$; Salata et al., 2000). Temperature ($^{\circ}\text{C}$) and pH were measured in the field.

The sample from the bottom of Lake Averno, a volcanic crater lake located a few hundred meters NW of the Monte Nuovo cone (Fig. 1a), was collected using a sampling equipment consisting of a Rilsan[®] tube (6 mm in diameter), lowered to the sampling depth, and an 150 mL syringe equipped with a three-way valve to pump the water up to the surface. The water sample was collected after the displacement of a water volume double that of the inner volume of the tube (Cabassi et al., 2013 and references therein).

The dissolved gas samples were collected into pre-evacuated 250 mL glass flasks, equipped with a Teflon stopcock, that were submerged into the water or connected to the Rilsan[®] tubes. The stopcock was opened to fill the vial of water up to about three quarters of its inner volume (Tassi et al., 2008, 2009).

3.2. Chemical and isotopic ($\delta^{13}\text{C}_{\text{TDIC}}$) analysis of waters

The main ionic species were analyzed by ion chromatography (IC), using an 861 Advanced Compact IC-Metrohm for cations (Na, NH_4 , K, Mg, Ca) and a 761 Compact IC-Metrohm for anions (F, Cl, Br, NO_3 , SO_4). The HCO_3 concentrations were determined by acidimetric titration (AT) with 0.01 N HCl using a Basic Titrino 794-Metrohm autotitrator. The analytical errors for IC and AT were $< 5\%$.

The analysis of $\delta^{13}\text{C}_{\text{TDIC}}$ (expressed in ‰ vs. V-PDB) was carried out with a Finnigan Delta Plus XL mass spectrometer on the CO_2 recovered after the reaction of 3 mL of water sample with 2 mL of anhydrous phosphoric acid *in vacuo* (Salata et al., 2000). The recovered CO_2 was analyzed after a two-step extraction and purification procedure on the gas mixture by using a N_2 and trichloroethylene solid-liquid mixture (e.g. Vaselli et al., 2006). The analytical error and the reproducibility for $\delta^{13}\text{C}_{\text{TDIC}}$ analysis were ± 0.05 ‰ and ± 0.1 ‰, respectively.

3.3. Chemical and isotopic ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$) analysis of dissolved gases

Inorganic gases (CO_2 , N_2 , O_2 , Ar and H_2) stored in the headspace of the sampling flasks were analyzed using a Shimadzu 15A and a Thermo Focus gas chromatographs equipped with Thermal Conductivity Detectors (TCD). Methane was analyzed using a Shimadzu 14A gas chromatograph equipped with a Flame Ionization Detector (FID). The chemical composition of the dissolved gas compounds was computed by considering the measured concentrations of gases stored in the headspace on the basis of: (i) headspace gas pressure and volume, (ii) volume of water in the flask and (iii) solubility coefficients of each gas compound (Whitfield, 1978).

The isotopic composition of dissolved CO_2 ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$, expressed in ‰ vs. V-PDB) was determined on the basis of the $^{13}\text{C}/^{12}\text{C}$ ratio measured in CO_2 from the sampling flask headspace ($\delta^{13}\text{C}_{\text{CO}_2\text{strip}}$). The $\delta^{13}\text{C}_{\text{CO}_2\text{strip}}$ was analyzed by using a Finnigan Delta Plus XL mass spectrometer after a two-step extraction and purification procedure, as described for the determination of the $\delta^{13}\text{C}_{\text{TDIC}}$ values. Both internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used in order to estimate the external precision. The analytical error and the reproducibility were ± 0.05 ‰ and ± 0.1 ‰, respectively. The $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values were calculated from the measured $\delta^{13}\text{C}_{\text{CO}_2\text{strip}}$ on the basis of the enrichment factor (ε_1) for gas-water isotope equilibrium proposed by Zhang et al. (1995):

$$\varepsilon_1 = \delta^{13}\text{C}_{\text{CO}_2(\text{aq})} - \delta^{13}\text{C}_{\text{CO}_2\text{strip}} = (0.0049 \times t) - 1.31 \quad (1)$$

where t ($^{\circ}\text{C}$) is the temperature.

4. Results

4.1. Campi Flegrei

4.1.1. Water geochemistry

The waters collected from the Campi Flegrei caldera showed heterogeneous physicochemical features (Table 1), with temperatures from 10 (#1) to 77 °C (#18), pH values from 6.20 (#10) to 8.27 (#13), TDS values from 722 (#8) to 19,066 mg/L (#18), and distinct geochemical facies, including Ca-HCO₃, Na-HCO₃, Na-Cl and Ca-Cl compositions (Fig. 2a).

The Ca-HCO₃ (#3 and #6) and Ca-Cl waters (#2) were characterized by low temperature (≤ 23 °C) and TDS values ($<1,000$ mg/L), whereas the Na-HCO₃ waters (#1, #4, #5, #7, #8, #9, and #12; Fig. 2a) displayed wide range of temperatures (from 10 to 63 °C) and TDS (from 795 to 4,330 mg/L).

The Na-Cl waters (#10, #11, #13, #14, #15, #16, #17, and #18; Fig. 2a) had relatively high temperatures (≥ 25 °C), with the exception of #13 (12 °C), and TDS values ($>1,000$ mg/L) (Table 1).

4.1.2. Chemical composition of dissolved gases

Atmospheric gases (P_{N_2} : from 215 to 1,231 mbar; P_{O_2} : from b.d.l. to 139 mbar; P_{Ar} : from 2.6 to 14 mbar), and carbon dioxide (PCO_2 varying from 0.8 to 54 mbar) dominate the chemical composition of the dissolved gases (Table 2; Fig. 3a). Methane and H₂ were relatively low (up to 0.12 and 0.14 mbar, respectively) with the exception of #13 (i.e. the sample from the bottom of Lake Averno) that was CH₄-rich (936 mbar) and characterized by the highest PH_2 value (9.8 mbar) among the whole Campi Flegrei water suite. Setting aside #4, all the waters with relatively high TDS values ($>2,000$ mg/L) were enriched in PCO_2 (from 4.7 to 54 mbar) (Table 2).

4.1.3. $\delta^{13}C_{TDIC}$ and $\delta^{13}C_{CO_2(aq)}$ values

The isotopic composition of dissolved CO₂ ($\delta^{13}C_{CO_2(aq)}$) varied from -23.7 (#6) to -5.0 (#10) ‰ vs. V-PDB (Table 3). Such a relatively large isotopic interval allowed to distinguish three groups of

waters (Table 4), as follows: A waters (from #1 to #8), i.e. those characterized by strongly negative $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values (≤ -19.7 ‰ vs. V-PDB) and low PCO_2 values (≤ 2.3 mbar; Fig. 3a); the isotopically heavy ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})} \geq -7.6$ ‰ vs. V-PDB) B waters (from #9 to #12), characterized by high TDS and PCO_2 values (up to 7,904 mg/L and 21 mbar, respectively) and Na-HCO₃ and Na-Cl compositions, and C waters (from #13 to #18), clustering in the Monte Nuovo area (Fig. 1a), with intermediate $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values (from -15.9 to -11.8 ‰ vs. V-PDB) with respect to those measured in the A and B waters.

The $\delta^{13}\text{C}_{\text{TDIC}}$ values (Table 3) were consistent with those of $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$: strongly negative values (from -16.2 to -12.8 ‰ vs. V-PDB) were measured in the A waters, whereas the highest $\delta^{13}\text{C}_{\text{TDIC}}$ values (from -1.6 to +0.4 ‰ vs. V-PDB) were related to the B waters (Table 4). The waters from the Monte Nuovo area (C waters) showed intermediate $\delta^{13}\text{C}_{\text{TDIC}}$ values (from -8.6 to -7.1 ‰ vs. V-PDB).

4.2. Vulcano Island

4.2.1. Water geochemistry

Similarly to the Campi Flegrei waters, those from Vulcano Island showed a relatively large range in temperature, pH and TDS varying from 21.5 (#19) to 51.8 °C (#27), from 5.61 (#23) to 8.27 (#36), and from 970 (#24) to 17,634 mg/L (#30), respectively (Table 1).

The two samples (#24 and #34) showing a Na-HCO₃ composition had relatively low temperatures and TDS values (≤ 26.3 °C and $\leq 1,520$ mg/L, respectively), whereas the Mg-HCO₃ water (#28; Fig. 2b) was at 47.2 °C and had a TDS of 4,589 mg/L. Those waters showing a Na-SO₄ composition (#22, #29, #31, #36, and #37; Fig. 2b) were characterized by temperatures and TDS values ranging from 27.4 to 48.5 °C and from 2,135 to 5,130 mg/L, respectively (Table 1). Temperature and TDS values of the Ca-SO₄ waters (#21, #23, #25, and #26; Fig. 2b) varied from 24 to 38.7 °C and from 1,260 to 3,863 mg/L, respectively (Table 1), whereas the Na-Cl waters (#19,

#20, #27, #30, #32, #33, #35, and #38; Fig. 2b) showed wide ranges of temperature (from 21.5 to 51.8 °C) and TDS values (from 1,020 to 17,634 mg/L).

4.2.2. Chemical composition of dissolved gases

Dissolved gases in the Vulcano waters (Table 2) mostly consisted of N₂ (from 215 to 1,017 mbar), O₂ (from 0.73 to 79 mbar), CO₂ (from 1.6 to 20 mbar) and Ar (from 1.3 to 12 mbar) (Fig. 3b). Most dissolved gases showed the presence of H₂, which reached 4.9 mbar at #23. *P*CH₄ was ≤ 0.14 mbar. The dissolved gas composition showed no clear relation with the water physicochemical features.

4.2.3. $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values

The $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values of dissolved gases from Vulcano Island ranged from -21.8 (#22) to -4.0 (#23) ‰ vs. V-PDB (Table 3). As observed for the Campi Flegrei samples, three different groups of waters were also distinguished at Vulcano (Table 4), as follows: isotopically light A waters (from #19 to #22), having the lowest *PCO*₂ values (≤ 2.3 mbar; Fig. 3b) and $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values ranging from -21.8 to -20.9 ‰ vs. V-PDB; B waters (from #23 to #28), mainly located at the base of La Fossa cone, characterized by *PCO*₂ values ≥ 13 mbar and $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ from -6.0 to -4.0 ‰ vs. V-PDB; C waters (from #29 to #38), with $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values, ranging from -16.5 to -9.1 ‰ vs. V-PDB, and *PCO*₂ values similar to those of the B waters (Table 2; Fig. 3b). The latter group of samples was collected both at the base of the volcanic edifice and in the northern and western portions of the Vulcano Porto Plain (Fig. 1a).

Similar to what observed at Campi Flegrei, the $\delta^{13}\text{C}_{\text{TDIC}}$ (Table 3) and the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values were strongly related, the former ranging from -17.5 to -14.5 ‰ vs. V-PDB, from -1.8 to +1.9 ‰ vs. V-PDB, and from -11.3 to -4.8 ‰ vs. V-PDB in the A, B, and C waters, respectively (Table 4).

5. Discussion

5.1. Campi Flegrei

5.1.1. Origin of waters and dissolved gases

The wide variation of chemical features characterizing the waters collected from the Campi Flegrei study area was interpreted as produced by mixing of fluids from different sources: (i) shallow aquifer(s) fed by meteoric water, (ii) seawater and (iii) deep geothermal brine (e.g. Baldi et al., 1975; Cortecchi et al., 1978; Duchi et al., 1995; Valentino et al., 1999; Valentino and Stanzione, 2003, 2004). The chemical composition of meteoric water permeating through the carbonates cropping out on the Apennine Chain (Duchi et al., 1995 and references therein; Valentino and Stanzione, 2003) varied from Ca-HCO_3 to Na-HCO_3 due to interaction with volcanic deposits. Close to the coastline (Fig. 1a), seawater contamination produced the Ca-Cl (#2) and Na-Cl (#4) waters characterized by low PCO_2 values (Table 2; Fig. 3a) and strongly negative $\delta^{13}\text{C}$ values of both $\text{CO}_{2(\text{aq})}$ and TDIC, approaching those related to microbial activity (Degens, 1969). Seawater inflow also affected the chemistry of #11, although for this water addition of deep Na-Cl fluids was also recognized (Valentino and Stanzione, 2003). A significant contribution of heat and fluids from the magmatic system was also characterizing the waters from the areas close to the Solfatara Crater (#12), Agnano (#9 and #10) and Monte Nuovo (from #13 to #18), as shown by their high PCO_2 values and the less negative carbon isotopic signatures (Tables 2 and 3). The relatively high HCO_3 concentrations measured in these waters were likely originated by dissolution of deep-sourced CO_2 , whereas their enrichment in NH_4 and Li (Table 1) indicate relatively high temperatures and prolonged water-rock interactions, respectively (Nicholson, 1993). Accordingly, their Li/Cl ratios points to those of the geothermal fluids exploited from wells drilled in the Mofete area (Guglielminetti, 1986) (Fig. 4). The relevant influence of the deep fluid source on the chemistry of #12 water was also supported by geophysical measurements showing that the Solfatara Crater corresponds to the major gas upflow zone of the Campi Flegrei hydrothermal system (Afanasyev et al., 2015). These data showed that the uprising of hot geothermal fluids is also affecting the Agnano Plain (De Siena et al., 2010), as confirmed by the chemical features of the hot and brackish #10 water (Table 1). Eventually, a highly permeable zone was recognized at the Monte Nuovo area (De

Siena et al., 2010; Petrillo et al., 2013), where the last eruptive event of the Campi Flegrei system occurred and the hottest and most saline water (#18) was found.

5.1.2. Processes regulating the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values

The wide-ranging carbon isotopic compositions observed at Campi Flegrei likely result from varying source contributions to the analyzed waters.

Both the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values and the low PCO_2 values in the *A* waters were consistent with those of interstitial soil water in areas not affected by degassing of deep-originated fluids (Degens, 1969; Faure, 1986; Clark, 2015). Consistently, the chemical composition of these waters, which are randomly distributed within the study area, pointed to a shallow (or marginal to the volcanic-hydrothermal system) source for the dissolved carbon species. Accordingly, they plotted close to the biogenic field in Fig. 5a, with $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ values approaching those expected for water interaction with biogenic CO_2 (Fig. 5b).

On the other hand, the chemical composition and the relatively high temperature, TDS and PCO_2 values shown by the *B* and *C* waters from the Solfatara, Agnano Plain, and Monte Nuovo areas clearly indicated a dominant contribution from hydrothermal fluids.

The $\delta^{13}\text{C}_{\text{TDIC}}$ vs. TDIC binary diagram (Fig. 5a) reports the theoretical field of the geothermal fluids that was drawn considering (i) the TDIC values of deep reservoir fluids collected from the Mofete geothermal wells (from 431 to 1,209 mmol/L; Allard et al., 1991 and references therein) and (ii) the $\delta^{13}\text{C}$ values of the fumarolic emissions in the Solfatara, Agnano Plain, and Monte Nuovo areas (from -1.9 to -0.6 ‰ vs. V-PDB; Vaselli et al., 2011; Tassi et al., 2015), assuming the isotopic composition of TDIC to be equal to that of $\text{CO}_{2(\text{g})}$. The latter assumption is supported by the fact that in the deep geothermal fluids feeding the fumarolic emissions the amount of dissolved CO_2 largely exceeds that of HCO_3 (Allard et al., 1991). Consequently, considering the HCO_3 in solution as being negligible with respect to $\text{CO}_{2(\text{aq})}$, a significant isotopic difference should not be expected between dissolved carbon and gaseous CO_2 in the hydrothermal system. Moreover, hydrothermal calcite, characterized by $\delta^{13}\text{C}$ values ranging from -3.1 to -2.4 ‰ vs. V-PDB, was found in the

Mofete drilling cores (Carella and Guglielminetti, 1983; Rosi and Sbrana, 1987; De Vivo et al., 1989; Caprarelli et al., 1997; Mormone et al., 2015). Considering an isotopic enrichment factor of about 2 ‰ between $\text{CO}_{2(g)}$ and calcite at the temperature measured in the geothermal wells (Bottinga, 1968), the precipitation of calcite under closed-system conditions in the deep hydrothermal reservoir would be related to gaseous CO_2 with $\delta^{13}\text{C}_{\text{CO}_{2(g)}}$ values from -1.1 to -0.4 ‰ vs. V-PDB, which were consistent with those measured in the fumarolic gases (e.g. Vaselli et al., 2011; Tassi et al., 2015).

Noteworthy, the *B* waters displayed $\delta^{13}\text{C}_{\text{TDIC}}$ values similar to those of the geothermal end-member (Fig. 5a), supporting the hypothesis that the chemistry of these waters was mainly controlled by the deep fluid source. Accordingly, these waters were collected from the central part of the caldera, where upwardly convecting fluid from the deep magmatic-hydrothermal system is particularly efficient.

The effects on $\delta^{13}\text{C}_{\text{CO}_{2(aq)}}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values of a simple gaseous CO_2 dissolution in a two-phase system can be checked by computing theoretical isotopic values of the C-bearing compounds in the liquid and gas phases. Initially, as gaseous CO_2 uprising from the deep reservoir dissolves into the shallow aquifers feeding the sampled wells, the produced $\text{CO}_{2(aq)}$ is expected to be enriched in ^{12}C relative to $\text{CO}_{2(g)}$, according to the equilibrium isotopic enrichment factor $\epsilon_{\text{CO}_{2(aq)}-\text{CO}_{2(g)}}$ defined by Deines et al. (1974), as follows:

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

where *T* is in K. Subsequently, $\text{CO}_{2(aq)}$ is converted to HCO_3^- , causing a further isotope fractionation, according to the isotopic enrichment factor $\epsilon_{\text{HCO}_3-\text{CO}_{2(aq)}}$ whose dependence on temperature was described by Mook et al. (1974), as follows:

$$\epsilon_{\text{HCO}_3-\text{CO}_{2(aq)}} = \frac{9866}{T} - 24.12 \quad (3)$$

Assuming (i) TDIC and HCO_3^- to be entirely derived from $\text{CO}_{2(g)}$ dissolution and $\text{CO}_{2(aq)}$ conversion, respectively, and (ii) the attainment of isotopic equilibrium between gaseous and

dissolved carbon species, the isotope mass balance can be used to define the $\delta^{13}\text{C}$ values of TDIC and $\text{CO}_{2(\text{aq})}$ resulting from $\text{CO}_{2(\text{g})}$ dissolution ($\delta^{13}\text{C}_{\text{TDIC}_{\text{dis}}}$ and $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}_{\text{dis}}}$, respectively), as follows:

$$\delta^{13}\text{C}_{\text{TDIC}_{\text{dis}}} = \varepsilon_{\text{CO}_{2(\text{aq})}-\text{CO}_{2(\text{g})}} + \delta^{13}\text{C}_{\text{CO}_{2(\text{g})}} \quad (4)$$

$$\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}_{\text{dis}}} = \delta^{13}\text{C}_{\text{TDIC}_{\text{dis}}} - \frac{\varepsilon_{\text{HCO}_3-\text{CO}_{2(\text{aq})}} \times \text{HCO}_3}{\text{TDIC}} \quad (5)$$

where HCO_3 and TDIC are in mmol/L.

Using the $\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}}$ values of the fumarolic emissions in eq. (4), the theoretical $\delta^{13}\text{C}_{\text{TDIC}_{\text{dis}}}$ values expected for hydrothermal CO_2 dissolution range from -2.8 to -1.5 ‰ vs. V-PDB, whereas the theoretical $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}_{\text{dis}}}$ values derived from eq. (5) at increasing $\text{HCO}_3/\text{CO}_{2(\text{aq})}$ ratios (i.e. proceeding of the $\text{CO}_{2(\text{aq})}$ to HCO_3 conversion; expressed in log values for graphical convenience) are depicted in Fig. 5b. These values were consistent with those measured in the *B* waters. In particular, the $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ value measured in the #12 sample, from the surroundings of the Solfatara Crater where the most intense hydrothermal gas upflow occurs, is to be considered the most intensely affected by carbon isotope fractionation caused by water-gas interaction processes. A shift towards values slightly higher than those expected for theoretical $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}_{\text{dis}}}$ was displayed by the #10 water, likely due to the occurrence of dissolved carbon species from both the uprising hydrothermal gases and the hot brine, an hypothesis supported by the relatively high contents of Cl, Li and NH_4 measured in this water.

Differently, the $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values in the *C* waters from the Monte Nuovo area were not consistent with a simple gas dissolution into shallow aquifers and were markedly lower than those measured in waters from both Solfatara and Agnano Plain areas. A mixing between geothermal fluids and the *A* waters, as suggested by Caliro et al. (2004) and apparently representing the most reliable explanation for the distribution of the *C* waters in Figs. 5a and 5b, is not consistent with the physicochemical features of #18. In fact, assuming (i) a shallow (or marginal) end-member having TDIC and $\text{CO}_{2(\text{aq})}$ of 6 and 0.05 mmol/L, respectively, and $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ of -16 and -25.8

‰ vs. V-PDB, respectively, and (ii) deep fluids with TDIC and $\text{CO}_{2(\text{aq})}$ of 431 and 430 mmol/L, respectively, and $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ of -1.25 ‰ vs. V-PDB, the $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values of the #18 water would imply a low geothermal fluid contribution (<2 %) that is not consistent with the chemical features of this water (Fig. 4), being the hottest and most saline among the analyzed samples. More likely, the negative shift observed in the *C* waters suggests that the uprising hydrothermal fluids were affected by secondary processes able to cause a ^{13}C - ^{12}C fractionation. Such processes, although widely occurring at different degrees throughout the caldera, were particularly efficient in the Monte Nuovo area, i.e. at the margin of the main hydrothermal fluids uplift area, where enhanced water-rock interaction, e.g. alteration of Ca-Al-silicates (Giggenbach, 1984), able to induce widespread calcite precipitation (Simmons and Christenson, 1994) occurs, as follows:



Chiodini et al. (2015a) suggested that the conversion of Ca-Al silicates into hydrothermal calcites (eq. (6)) is actually responsible for a significant CO_2 sequestration in the Campi Flegrei caldera, as also supported by the already mentioned occurrence of hydrothermal calcite in the Mofete drillings. The isotopic fractionation caused by calcite precipitation occurring during hydrothermal fluid circulation under open-system conditions can be described as a Rayleigh-type fractionation process, as follows:

$$\delta^{13}\text{C}_{\text{TDIC}_{\text{res}}} = [(\delta^{13}\text{C}_{\text{TDIC}_{\text{ini}}} + 1000) \times f^{(\alpha_{\text{calcite-TDIC}} - 1)}] - 1000 \quad (7)$$

where $\delta^{13}\text{C}_{\text{TDIC}_{\text{ini}}}$ is the initial isotopic composition of TDIC in the hydrothermal fluid, $\delta^{13}\text{C}_{\text{TDIC}_{\text{res}}}$ is the isotopic composition of the residual TDIC after calcite precipitation, f is the fraction of residual TDIC and $\alpha_{\text{calcite-TDIC}}$ is the isotopic fractionation factor between calcite and TDIC computed, as follows:

$$\alpha_{\text{calcite-TDIC}} - 1 = \frac{\varepsilon_{\text{calcite-TDIC}}}{1000} = \frac{\varepsilon_{\text{calcite-CO}_2(\text{g})} - \varepsilon_{\text{TDIC-CO}_2(\text{g})}}{1000} =$$

$$= \left[\varepsilon_{\text{calcite}-\text{CO}_2(\text{g})} - \left(\frac{\text{CO}_{2(\text{aq})}}{\text{TDIC}} \times \varepsilon_{\text{CO}_2(\text{aq})-\text{CO}_2(\text{g})} \right) + \left(\frac{\text{HCO}_3}{\text{TDIC}} \times \varepsilon_{\text{HCO}_3-\text{CO}_2(\text{g})} \right) \right] \times 10^{-3} \quad (8)$$

The $\varepsilon_{\text{CO}_2(\text{aq})-\text{CO}_2(\text{g})}$ value was calculated as in eq. (2), whereas $\varepsilon_{\text{HCO}_3-\text{CO}_2(\text{g})}$ and $\varepsilon_{\text{calcite}-\text{CO}_2(\text{g})}$ were calculated using the equations proposed by Deines et al. (1974), as follows:

$$\varepsilon_{\text{HCO}_3-\text{CO}_2(\text{g})} = \delta^{13}\text{C}_{\text{HCO}_3} - \delta^{13}\text{C}_{\text{CO}_2(\text{g})} = \frac{1099000}{T^2} - 4.54 \quad (9)$$

$$\varepsilon_{\text{calcite}-\text{CO}_2(\text{g})} = \delta^{13}\text{C}_{\text{calcite}} - \delta^{13}\text{C}_{\text{CO}_2(\text{g})} = \frac{1194000}{T^2} - 3.63 \quad (10)$$

The theoretical $\delta^{13}\text{C}_{\text{TDIC}_{\text{res}}}$ values were computed according to the following assumptions: (i) the $\delta^{13}\text{C}_{\text{TDIC}_{\text{ini}}}$ value was equal to that of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ reported for the Monte Nuovo fumarole (-1.4 ‰ vs. V-PDB; Vaselli et al., 2011), (ii) fixed near-neutral pH conditions, consistent with those reported for geothermal brines at depth (Carella and Guglielminetti, 1983), and (iii) temperatures ranging from 80 to 100 °C. As shown in Fig. 6, progressive calcite precipitation efficiently decreases the $\delta^{13}\text{C}_{\text{TDIC}_{\text{res}}}$ values. Hence, a Rayleigh-type fractionation process induced by calcite precipitation from hydrothermal fluids under open-system conditions can explain the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values of the *C* waters. Accordingly, although affected by secondary processes, the dissolved carbon species of the #18 sample likely had a hydrothermal origin, in contrast with the low hydrothermal contribution (<2%) estimated on the basis of the mixing model (Fig. 5a) between geothermal fluids and shallow waters.

5.2. Evidences from Vulcano Island

The hydrogeological setting in Vulcano Island is characterized by discontinuous shallow aquifers, complex vertical and horizontal flow paths and different fluid sources (meteoric water, seawater, uprising geothermal waters and volcanic steam) (e.g. Capasso et al., 1999, 2001; Cortecchi and Boschetti, 2001; Cortecchi et al., 2001; Boschetti et al., 2003; Federico et al., 2010; Madonia et al., 2015), producing strongly differing geochemical features in the well waters (Table 1).

Similar to what was observed at Campi Flegrei, the *A* waters displayed both chemical (relatively low TDS, dissolved gases dominated by N_2 , PCO_2 values in the range of soil CO_2) and isotopic ($\delta^{13}C\text{-}CO_{2(aq)}$ and $\delta^{13}C_{TDIC}$ values consistent with those of organic-derived carbon) features compatible with aquifers fed by meteoric waters with a negligible influence of volcanic gases (Figs. 7a and 7b).

Conversely, the chemistry of the *B* waters, including most wells from the base of La Fossa cone, were interpreted as produced by interaction of uprising hot steam and mature geothermal fluids (Capasso et al., 1999, 2000, 2001; Boschetti et al., 2003). A relevant contribution from volcanic condensates was recognized in #27 well, where temporal variations in PCO_2 values were found to be strikingly related to changes in La Fossa crater fumarolic activity (Capasso et al., 1999, 2000). Accordingly, the supply of volcanic fluids was highlighted by the presence of a piezometric high (Madonia et al., 2015) and anomalous CO_2 soil degassing (Capasso et al., 2000) in this area. Similarly, the relatively high temperature, the TDS values of Cl^- and SO_4 -rich waters from Baia di Levante (#23, #25, #26) and the peculiarly high HCO_3 contents measured in the #28 water (Table 1; Capasso et al., 2000, 2001; Boschetti et al., 2003) were likely originated by interaction processes with volcanic condensates or CO_2 -rich steam phase. Accordingly, both the measured (i) $\delta^{13}C_{TDIC}$ values (Fig. 7a), which approached those of the $\delta^{13}C_{CO_2}$ in fumarolic and bubbling gases at La Fossa crater and Baia di Levante (from -3.4 to +0.7 ‰ vs. V-PDB; Capasso et al., 1997), and (ii) $\delta^{13}C_{CO_{2(aq)}}$ values, which were consistent with the theoretical $\delta^{13}C_{CO_{2(aq)}_dis}$ values derived from eqs. (4) and (5) assuming dissolution of gaseous CO_2 with $\delta^{13}C$ values in the fumarolic range (Fig. 7b), confirmed a strong interaction of the *B* waters with high temperature fluids from the deep volcanic system. Indeed, the foot of the volcanic cone and Baia di Levante represent zones of structural weakness where volcanic and hydrothermal fluids are mainly drained by fracture/faulting systems, resulting in both fumarolic discharges and intense CO_2 soil degassing at the surface.

Noteworthy, most *C* waters were similarly located along a NE-oriented alignment corresponding to the Tindari-Letojanni fault (Fig. 1b; Billi et al., 2006), i.e. the main tectonic discontinuity in this

region, where an upflow of volcanogenic fluids was inferred on the basis of an anomalous elevation of the water table recognized in this area (Inguaggiato et al., 2012; Madonia et al., 2015). The remaining *C* waters (#30 and #33), characterized by high Cl, Br, NH_4 and Li contents (Table 1) and Na/Cl and Cl/Br mass ratios (0.51 and 302 in #30 and 0.57 and 313 in #33, respectively) similar to those of seawater (Na/Cl = 0.56, Cl/Br = 292), likely intercepted a seawater-contaminated water body affected by hydrothermal contribution (Federico et al., 2010).

Despite the well-assessed contribution from hydrothermal fluids, the values of TDIC and $\text{CO}_{2(\text{aq})}$ measured in the *C* waters were ascribable to neither pure dissolution of deep-derived CO_2 into shallow aquifers, as shown in Fig. 7b, nor simple mixing model between hydrothermal fluids and biogenic carbon sources. This would not indeed be consistent with the relatively high PCO_2 and TDIC values and the high Cl, Br, NH_4 and Li contents (up to 8,463, 28, 15 and 5.2 mg/L, respectively; Table 1) of these waters, which are unequivocal hints of a relevant contribution from hydrothermal fluids. As previously demonstrated for the case study of Campi Flegrei, a strong isotopic fractionation can be easily produced by a Rayleigh-type calcite precipitation affecting the uprising deep fluids (Fig. 6). The occurrence of calcite precipitation, coupled with steam condensation and multi-step boiling processes, was already suggested by Federico et al. (2010) to explain the wide variations in major ions, dissolved gases and stable isotopes in thermal waters from the island. Although such process is not expected to occur only along the Tindari-Letojanni fault, local conditions may play a key role in determining the isotopic composition of dissolved carbon species in thermal waters. In particular, (i) decreasing temperature and salinity (Madonia et al., 2015) at increasing distance from the volcanic edifice and (ii) absence of CO_2 soil degassing anomalies in this area (Inguaggiato et al., 2012) revealed a less intense supply of volcanic/hydrothermal fluids into shallow ground waters, which, consistently with what observed at the Campi Flegrei, likely allowed secondary isotopic fractionation processes to overwhelm the typical signature of the deep-derived carbon.

6. Conclusions

The chemical and isotopic compositions of the main solutes and dissolved gases in thermal and cold waters collected from wells located at Campi Flegrei and Vulcano Island were investigated to elucidate the processes controlling the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values. The occurrence of hydrothermal-magmatic CO_2 , possibly affected by a relatively low isotopic fractionation due to dissolution in shallow water, exhaustively explains the chemical features of the wells located in the proximity of the areas interested by the highest deep fluid upflow, corresponding to the Solfatara crater and La Fossa cone at Campi Flegrei and Vulcano Island, respectively. In some cases (e.g. the well waters from Agnano Plain), the involvement of both hydrothermal gases and geothermal brine should be invoked to reconcile the measured and theoretical data.

Waters dominantly fed by shallow meteoric aquifers were occurring in the two volcanic systems and characterized by dissolved CO_2 and TDIC showing the typical chemical and isotopic features of interstitial soil waters. Water samples with intermediate $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values from both areas are the main point of interest of this study, since their chemistry is not consistent with a simple mixing between deep and shallow end-members. Instead, assuming a dominant deep source for the C-bearing species of these waters, we demonstrated that the strong isotope fractionation ($>5\%$) necessary to explain the measured isotopic values can be obtained through Rayleigh-type calcite precipitation. This excludes a significant contribution from the shallow source, as dictated by the classical mixing model that would lead to a strong underestimation of the deep CO_2 fraction. At Campi Flegrei, these waters were only found at Monte Nuovo. The cause of this peculiar relationship between the spatial distribution and the chemical features of these waters, although intriguing, is not clear and deserves further investigation. Notwithstanding, it is worth noting that calcite precipitation is commonly observed in volcanic and hydrothermal systems, hence the hypothesized secondary ^{13}C - ^{12}C fractionation process can be considered to play a fundamental role in controlling the isotopic signature of carbon in dissolved CO_2 and TDIC at a global scale. These

findings imply that intermediate $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ values are to be interpreted with extreme caution for the assessment of the carbon budget of hydrothermal-volcanic systems. As assessed for the Campi Flegrei waters, the attribution of such carbon isotopic values to mixing between shallow ground waters and deep-originated fluids could be misleading, determining a substantial underestimation of the hydrothermal contribution to dissolved carbon species in thermal waters.

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Table captions

Table 1. Chemical composition of the main solutes (anions and cations, in mg/L), temperature (°C), pH and salinity (expressed as TDS, in mg/L) of water samples collected from Campi Flegrei and Vulcano Island.

Table 2. Chemical composition of the main gases dissolved in waters (partial pressures in mbar) from Campi Flegrei and Vulcano Island.

Table 3. $\delta^{13}\text{C}$ (in ‰ vs. V-PDB) of dissolved CO_2 and TDIC in waters from Campi Flegrei and Vulcano Island.

Table 4 Ranges of isotopic and chemical signatures of the three water groups (*A*, *B* and *C*) distinguished among samples from Campi Flegrei and Vulcano Island.

Figure captions

Fig. 1. Satellite photos of (a) Campi Flegrei caldera and (b) Vulcano Island. The sampling sites of thermal waters are reported. Symbols are according to the three groups of waters distinguished on the basis of the dissolved CO_2 isotopic composition, as follows: group *A* = white squares; group *B* = dark grey diamonds; group *C* = light grey circles (see the text for details). The Tindari-Letojanni (LT) Fault is shown in Fig. 1b (white dashed line).

Fig. 2. Ternary diagrams for the main anions (HCO_3 , Cl , SO_4) and cations (Ca , Mg , Na+K) from (a) Campi Flegrei caldera and (b) Vulcano Island. In Fig. 2a, the composition of local seawater (black asterisk) and geothermal fluids from Mofete drillings (black triangles) at Campi Flegrei (Fig. 1a), as reported by Guglielminetti (1986), is also shown.

Fig. 3. PCO_2 - PN_2 - PO_2 ternary diagrams for dissolved gases in waters from (a) Campi Flegrei caldera and (b) Vulcano Island. The straight line corresponds to the N_2/O_2 ratio in Air Saturated Water (ASW).

Fig. 4. Li vs. Cl (in mg/L) binary diagram for waters from Campi Flegrei caldera. Symbols as in Fig. 2a.

Fig. 5. (a) $\delta^{13}C_{TDIC}$ vs. TDIC (in mmol/L) and (b) $\delta^{13}C_{CO_2(aq)}$ vs. $\log(HCO_3/CO_{2(aq)})$ binary diagrams for waters from Campi Flegrei caldera. The mixing line between a biogenic end-member and deep geothermal fluids is shown (black dash dot line) in both (a) and (b). The fraction (in percentage) of the geothermal fluids involved in the mixture is reported. Note that the mixing between biogenic and geothermal end-members, although apparently compatible with waters distribution in (a), is not a viable explanation for the chemical composition of C waters (see text for details). In (b), the mixing line between the #12 sample and geothermal fluids (black dot line) is also shown. The $\delta^{13}C_{CO_2(aq)_dis}$ values at increasing conversion of $CO_{2(aq)}$ to HCO_3 for waters with $\delta^{13}C_{TDIC}$ derived from dissolution of hydrothermal CO_2 , i.e. $\delta^{13}C_{TDIC_dis}$ from -2.8 to -1.5 ‰ vs. V-PDB (straight and dash lines, respectively), are depicted in (b) for different temperatures (60 °C = black lines; 70 °C = blue lines; 80 °C = green lines; 90 °C = red lines).

Fig. 6. Theoretical $\delta^{13}C_{TDIC}$ values produced by calcite precipitation (f = fraction of residual TDIC after precipitation) computed for different temperatures (80 °C = solid line; 90 °C = dashed line; 100 °C = dot line) and fixed pH values.

Fig. 7. (a) $\delta^{13}C_{TDIC}$ vs. TDIC (in mmol/L) and (b) $\delta^{13}C_{CO_2(aq)}$ vs. $\log(HCO_3/CO_{2(aq)})$ binary diagrams for waters from Vulcano Island. The $\delta^{13}C_{CO_2(aq)_dis}$ values at increasing conversion of $CO_{2(aq)}$ to HCO_3 for waters with $\delta^{13}C_{TDIC}$ derived from dissolution of hydrothermal CO_2 , i.e. $\delta^{13}C_{TDIC_dis}$ from -4.26 to -0.15 ‰ vs. V-PDB (straight and dash lines, respectively), are depicted in (b) for different

temperatures (50 °C = purple lines; 60 °C = black lines; 70 °C = blue lines; 80 °C = green lines; 90 °C = red lines).

ACCEPTED MANUSCRIPT

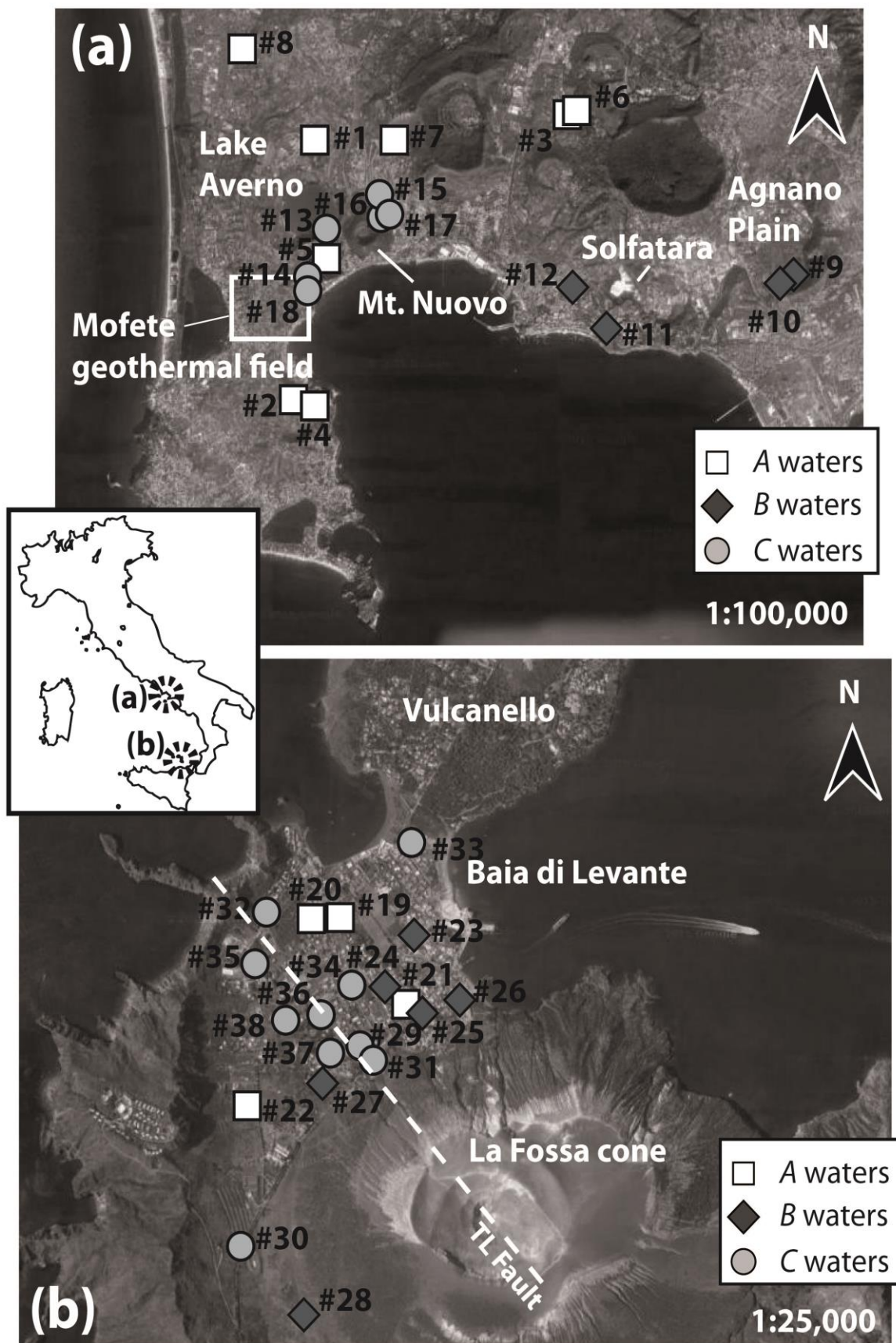


Fig. 1

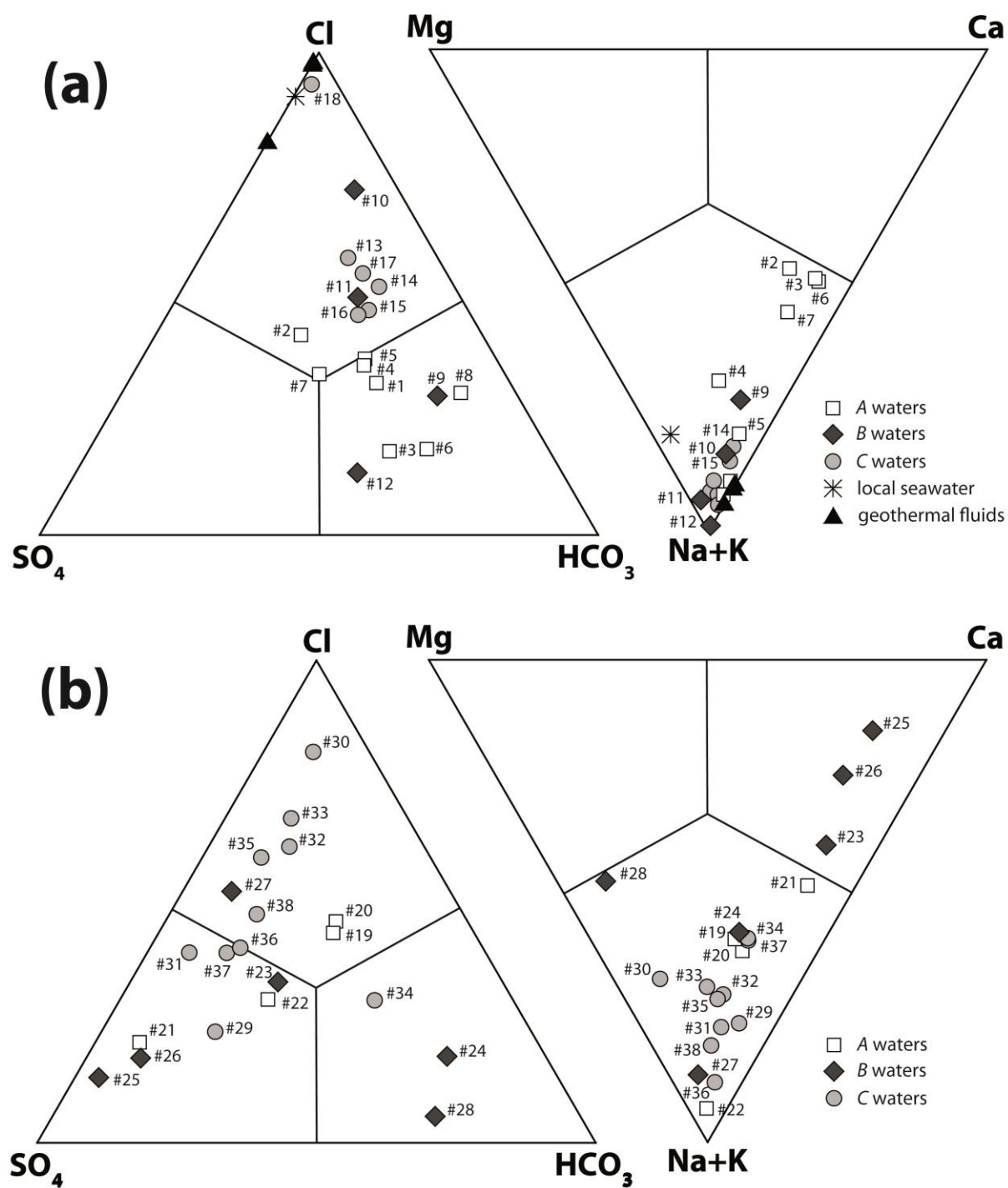


Fig. 2

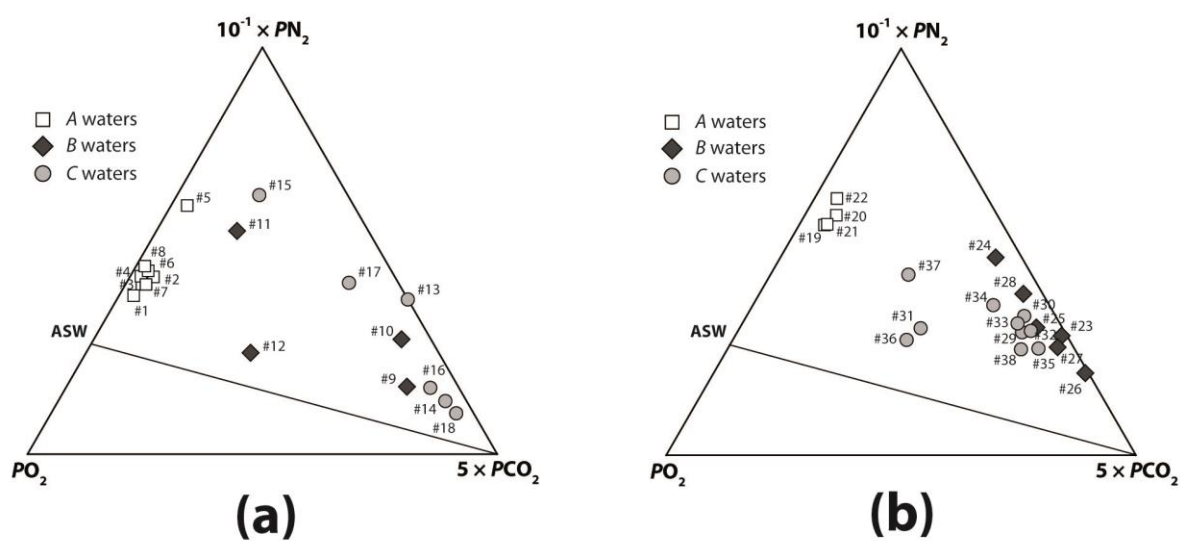


Fig. 3

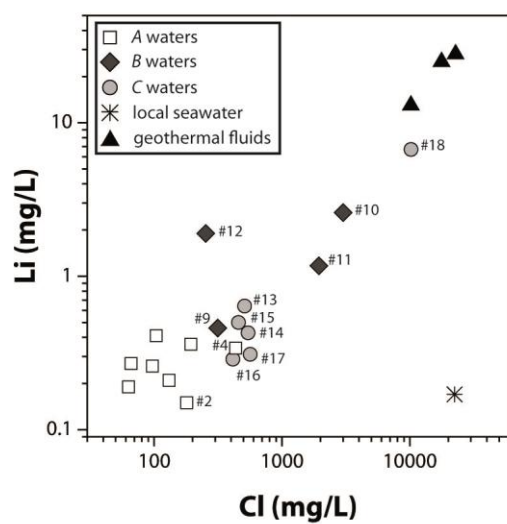


Fig. 4

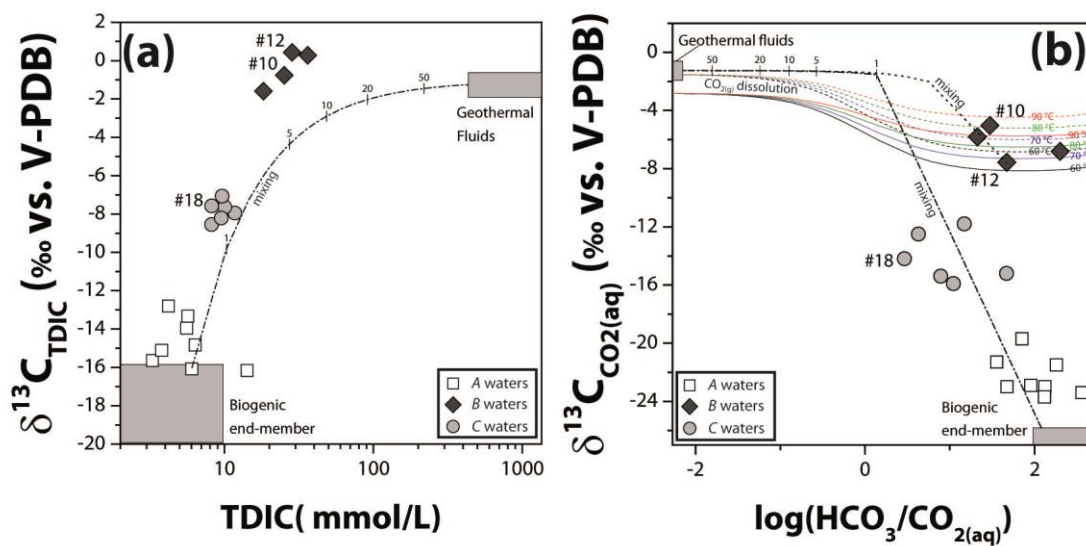


Fig. 5

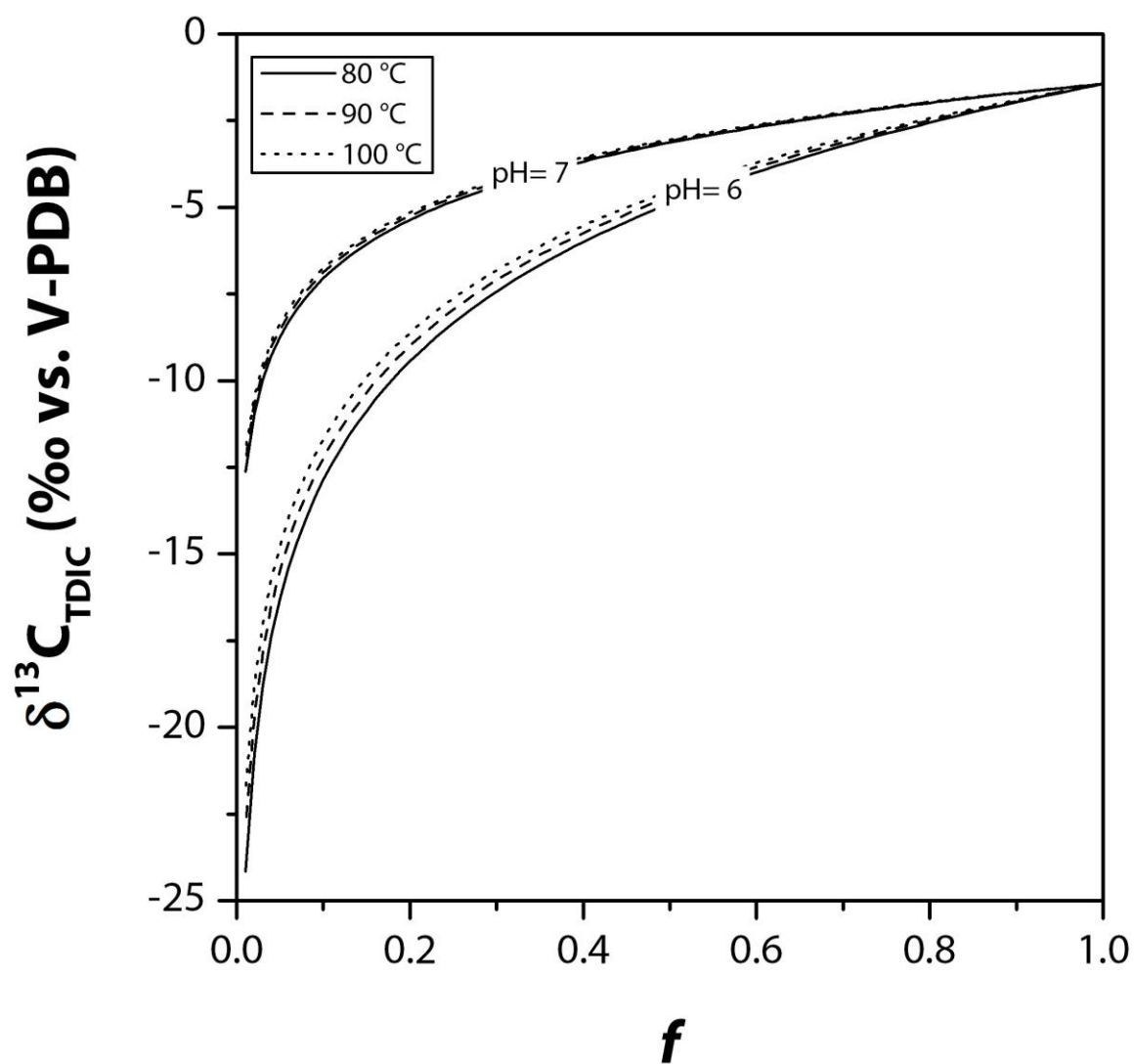


Fig. 6

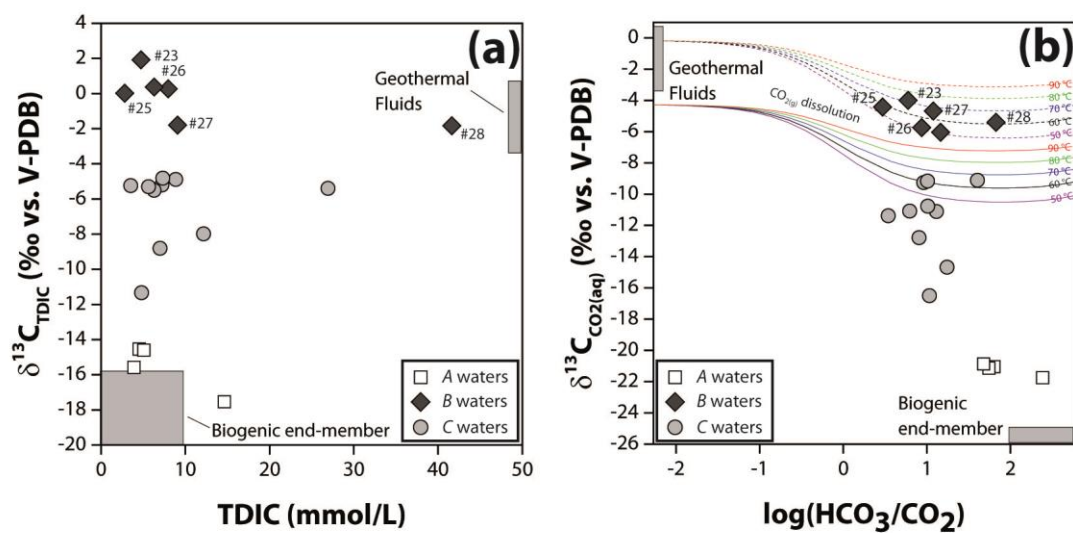


Fig. 7

Table 1

Study area	E (UTM)	N (UTM)	I D	name	gro up	T	pH	TD S	HCO ₃ ⁻	F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Li ⁺
Campi Flegrei	422236	4522378	1	Vivai e Piante	A	10	7.99	795	253	11.52	104	0.22	59	107	20	1.8	210	27	0.27	0.41
	421823	4518191	2	Agriturismo di Baia	A	11	7.12	997	195	0.97	180	0.53	120	191	119	22	122	45	0.31	0.15
	426565	4522770	3	Catone	A	19	7.30	851	337	4.40	63	1.14	60	141	97	9.2	84.0	54	0.61	0.19
	422131	4518162	4	Castello di Baia	A	21	7.07	3027	862	4.04	435	1.53	383	408	150	72	623	88	0.16	0.34
	422368	4520460	5	Costagliola	A	22	7.20	1163	366	5.72	194	0.52	66	169	48	8.7	245	60	0.11	0.36
	426651	4522845	6	Rist. Edera	A	23	7.32	802	385	3.75	66	0.97	5.60	109	91	7.5	80.0	52	1.3	0.27
	423664	4522351	7	Parco Delta	A	30	7.58	1056	226	2.95	131	0.31	211	177	104	15	160	28	0.24	0.21
	421045	4523852	8	Parco Enea	A	37	6.77	722	344	12.1	97	0.86	0.01	44	12	1.4	182	28	0.63	0.26
	430331	4520074	9	Agnano Marte	B	21	6.46	2317	1064	4.65	314	0.85	1.6	212	121	30	450	116	2.9	0.46
	430259	4520013	10	Agnano De Pisis	B	55	6.20	7866	1488	2.74	3009	11	0.92	448	279	75	2209	330	9.5	2.6
	427172	4519315	11	Terme Puteolane	B	58	6.90	7904	2196	4.96	1944	5.12	31	984	46	67	2434	186	4.5	1.2
	426602	4519946	12	Tortorelli	B	63	7.16	4330	1699	14.73	253	0.42	7.0	972	11	2.0	1187	182	0.15	1.9
	422375	4521003	13	Averno Lake	C	12	8.27	1753	405	9.07	510	1.17	0.94	193	25	13	536	60	0.44	0.64
	422151	4520287	14	Samuele	C	25	7.46	2104	636	7.19	543	1.00	2.13	193	82	17	520	103	0.12	0.43
	423382	4521520	15	Esposito	C	36	7.55	2158	601	5.62	457	1.35	108	236	70	13	541	124	0.25	0.50

	423323	452116 4	1 6	Ippico	C	36	7.7 8	197 9	533	7.4 0	413	0.6 3	120	247	34	14	484	12 5	0.29	0.2 9
	423436	452123 2	1 7	Damiani	C	46	7.4 5	221 6	552	8.3 6	565	2.0 2	94	212	36	8.6	611	12 7	0.23	0.3 1
	422057	451998 3	1 8	Stufe di Nerone	C	77	6.5 5	190 66	373	17. 02	102 27	36	89	683	30 1	45	709 4	19 3	1.5	6.7
Vulcano Island	495989	425195 7	1 9	Casa con Pesci	A	21. 5	7.3 2	102 0	272	7.3 6	220	0.3 2	39	173	74	28	167	38	0.97	
	495858	425194 6	2 0	Casa Rosa	A	21. 7	7.3 1	113 9	305	13. 6	266	0.4 4	8.6	185	85	27	195	53	0.42	
	496281	425158 5	2 1	Piscio'	A	37. 8	6.4 6	327 4	234	5.0 1	356	0.5 8	23	165 1	40 4	48	395	15 7	0.61	
	495582	425116 4	2 2	Lentia	A	47. 1	7.4 9	398 7	889	16 579	1.8 2	10	115 7	35	24	926	34 7	2.2	0.3 7	
	496316	425187 3	2 3	Bambara	B	24. 6	5.6 1	126 0	247	6.7 7	181	0.4 8	135	296	18 9	21	130	51	2.4	
	496193	425166 3	2 4	Casamento	B	26. 3	5.8 7	970	454	4.2 8	73.3	0.0 2	36	98	73	26	126	79	0.75	
	496347	425155 7	2 5	Rifici	B	30	7.1 4	345 4	128	4.9 4	236	0.3 6	120	194 2	73 0	80	111	10 1	0.8	0.1 7
	496520	425160 4	2 6	Rimessa	B	38. 7	5.8 9	386 3	344	4.8 5	360	0.5 8	0.24	201 8	67 9	91	206	15 8	1.4	0.3 5
	495922	425125 2	2 7	Camping Sicilia	B	51. 8	8.1	624 5	510	11. 3	176 0	4.2 7	1.89	179 0	95	95	148 7	48 8	2.2	0.7 7
	495826	425028 7	2 8	Discarica	B	47. 2	6.8 6	458 9	2503	11. 5	116	0.1 9	0.28	748	10 4	326	404	37 5	0.93	
	496088	425141 8	2 9	Genovese	C	46	7.1 2	231 9	398	11	261	0.4 6	35	869	11 0	25	417	19 2	0.22	
	495547	425058 7	3 0	Eas	C	46. 5	6.6 6	176 34	1604	12. 3	846 3	28	1.4	142 5	50 0	921	432 7	33 2	15	5.2
	496132	425138 5	3 1	Chantal	C	48. 5	6.9 8	513 0	350	6.0 6	106 2	2.2 4	3.4	193 6	21 6	87	109 9	36 6	1.6	0.8 2
	495661	425198 5	3 2	Eden Park	C	23. 9	7.0 1	129 6	167	22	411	0.7 8	32	219	69	29	243	10 2	0.68	0.1 6
	496305	425226 4	3 3	Eros	C	24	6.9 4	602 4	703	14. 2	231 6	7.4	0.75	974	29 5	182	131 1	21 1	9	0.4 4

	496037	425167 4	3 4	Le Palme	C	25. 2	7.1 3	152 0	503	14. 6	189	0.3 6	148	215	10 7	32	195	93	23	0.0 7
	495615	425176 9	3 5	Orsa Maggiore	C	27. 1	7.2 9	314 2	297	15. 3	967	1.6 5	105	671	15 9	76	663	18 4	2.3	0.5 6
	495896	425155 6	3 6	Davanti Casa Schmidt	C	27. 4	8.2 7	289 6	407	12. 1	591	1.1 5	32	860	60	24	653	25 4	1.4	
	495940	425139 6	3 7	Le Calette	C	38. 9	6.9 8	213 5	269	8.4	431	1.1	52	688	17 0	50	314	15 0	1.3	0.3
	495748	425153 0	3 8	Bonanno	C	40. 3	7.6 9	268 6	380	13. 7	669	1.4 6	3.66	707	82	44	596	18 7	2.3	0.3 7

Table 2

Study area	ID	group	PCO_2	PN_2	PO_2	PAr	PCH_4	PH_2	P_{total}
Campi Flegrei	1	A	1.5	931	139	11	0.039		1,082
	2	A	2.3	988	117	11	0.026		1,118
	3	A	1.6	945	124	11	0.039		1,081
	4	A	1.0	945	117	11	0.032		1,073
	5	A	1.2	1,031	60	12	0.12		1,104
	6	A	1.2	888	102	9.3	0.026		1,000
	7	A	2.0	959	124	10	0.019		1,095
	8	A	0.80	974	109	11	0.032		1,094
	9	B	21	243	16	2.7	0.045		283
	10	B	21	458	10	5.2	0.006	0.050	495
	11	B	4.7	745	38	8.6	0.032	0.100	796
	12	B	15	544	88	6.2	0.019	0.038	653
	13	C	40	1,231		14	936	9.8	2,231
	14	C	34	272	9.5	3.3	0.058	0.100	319
	15	C	5.4	988	29	11	0.032		1,034
	16	C	20	215	8.0	2.6	0.078	0.063	246
	17	C	16	702	18	7.3	0.071	0.075	742
	18	C	54	315	12	3.7	0.026	0.14	385
Vulcano Island	19	A	1.8	945	63	11	0.14		1,022
	20	A	2.3	1,017	59	12	0.084		1,090
	21	A	2.1	988	65	11	0.078		1,066
	22	A	1.6	1,017	52	11	0.097		1,081
	23	B	18	372	1.5	3.3	0.019	4.9	400
	24	B	13	702	8.0	8.0	0.032	0.96	732
	25	B	18	458	8.0	5.3	0.006	1.2	491
	26	B	17	215	0.73	1.3	0.013	2.4	236
	27	B	18	344	4.4	4.0	0.058	3.4	374
	28	B	16	558	5.8	4.6	0.039	0.74	585
	29	C	18	458	14	4.6	0.006	1.1	496
	30	C	17	487	9.5	4.6	0.032	0.85	519
	31	C	15	587	57	4.6	0.013	0.61	664
	32	C	20	501	12	4.6	0.013	1.2	539
	33	C	17	472	13	4.6	0.013	0.96	508
	34	C	16	587	19	6.6	0.026	0.74	630
	35	C	20	401	12	4.0	0.006	0.36	437
	36	C	17	644	79	5.3	0.013	0.51	746
	37	C	11	802	47	8.6	0.019	0.44	869
	38	C	20	415	18	4.0	0.032	0.64	458

Table 3

Study area	ID	group	$\delta^{13}\text{C}_{\text{CO2(aq)}}$	$\delta^{13}\text{C}_{\text{TDIC}}$
Campi Flegrei	1	A	-19.7	-12.8
	2	A	-21.3	-15.7
	3	A	-22.9	-14.0
	4	A	-23.4	-16.2
	5	A	-23.0	-16.1
	6	A	-23.7	-14.8
	7	A	-23.0	-15.1
	8	A	-21.5	-13.3
	9	B	-5.8	-1.6
	10	B	-5.0	-0.8
	11	B	-6.8	0.3
	12	B	-7.6	0.4
	13	C	-12.5	-8.6
	14	C	-15.4	-8.0
	15	C	-15.2	-7.6
	16	C	-15.9	-8.2
	17	C	-11.8	-7.1
	18	C	-14.2	-7.6
Vulcano Island	19	A	-21.0	-14.5
	20	A	-21.1	-14.6
	21	A	-20.9	-15.6
	22	A	-21.8	-17.5
	23	B	-4.0	1.9
	24	B	-6.0	0.3
	25	B	-4.4	0.0
	26	B	-5.7	0.4
	27	B	-4.7	-1.8
	28	B	-5.4	-1.8
	29	C	-9.3	-5.2
	30	C	-9.1	-5.4
	31	C	-9.2	-5.5
	32	C	-11.4	-5.2
	33	C	-14.7	-8.0
	34	C	-11.1	-4.9
	35	C	-11.1	-5.3
	36	C	-10.8	-4.8
	37	C	-16.5	-11.3
	38	C	-12.8	-8.8

Table 4

Study area	group	PCO_2 (mbar)		$\delta^{13}C_{CO2(aq)}$ (‰ vs. V-PDB)		TDIC (mmol/L)		$\delta^{13}C_{TDIC}$ (‰ vs. V-PDB)	
		min	max	min	max	min	max	min	max
Campi Flegrei	A	0.8	2.3	-23.7	-19.7	3.29	14.17	-16.2	-12.8
	B	4.7	21	-7.6	-5.0	18.26	36.18	-1.6	0.4
	C	5.4	54	-15.9	-11.8	8.19	11.76	-8.6	-7.1
Vulcano Island	A	1.6	2.3	-21.8	-20.9	3.92	14.63	-17.5	-14.5
	B	13	18	-6.0	-4.0	2.81	41.64	-1.8	1.9
	C	11	20	-16.5	-9.1	3.53	26.95	-11.3	-4.8

Highlights

- Natural waters from Campi Flegrei and Vulcano Island were analyzed
- $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ ranged between hydrothermal and biogenic end-members
- Gas chemical composition excluded mixing between hydrothermal and shallow waters
- The isotopic signature of hydrothermal fluids was affected by secondary processes
- These processes may strongly affect the hydrothermal/magmatic CO_2 budget estimates