



## Chemical and isotopic characterization of groundwater and thermal waters from the Campi Flegrei caldera (southern Italy)

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### ABSTRACT

We report here on the results of an extensive hydrogeochemical survey of the chemical and isotopic composition of thermal groundwater in the Campi Flegrei caldera (CFC), a restless volcanic system in the Campania Volcanic Province of Southern Italy. Our hydrogeochemical study, based on the collection of 114 groundwater samples, is the first comprehensive one since uplift, seismicity and degassing resumed in 2005, continuing today at accelerating rate. We use our results to characterize the processes that control the wide diversity of groundwater composition observed. We identify a set of key source processes governing the composition of the CFC thermal waters: i) the infiltration of meteoric water, responsible for the formation of diluted cold groundwater having bicarbonate as the prevalent anion (fresh waters), ii) mixing, upon downward infiltration in the aquifer(s), with high-temperature hydrothermal reservoir brines of probable marine origin (chloride waters), iii) the dissolution of a CO<sub>2</sub>-He rich magmatic-hydrothermal gas, with isotopic signature (respectively  $\delta^{13}\text{C} \sim -1\text{‰}$  vs. PDB and  $^3\text{He}/^4\text{He} \sim 3\text{Ra}$ , where Ra is the atmospheric He isotope ratio) similar to the Solfatara hydrothermal gases, generating bicarbonate-rich groundwater; (iv) near-surface dilution by hot condensates, formed by partial condensation of H<sub>2</sub>S-rich Solfatara like hydrothermal steam, generating sulphate-rich steam heated waters. In near-surface environments, upward migrating groundwater also degases, releasing poorly soluble gas compounds (He, Ar, N<sub>2</sub>, CH<sub>4</sub>) and becoming enriched in more soluble CO<sub>2</sub>. The above processes can work in concert, but each dominates in specific regions of the hydrothermal system, hence causing the extreme spatial diversity of water chemistry observed within the caldera. Our conceptual model for the processes acting within the thermal groundwater system will be crucial to interpreting any temporal change in groundwater chemistry observed in the installed permanent (instrumental) groundwater-monitoring network, which is critically needed for improving geochemical volcano monitoring during current acceleration of the unrest.

### 1. Introduction

Active volcanoes are sites of intense hydrothermal circulation, driven by mass/heat exchange between shallow infiltrated (meteoric/marine) waters and magmatic volatiles sourced by magma stored within the transcrustal magmatic plumbing system (Goff and Janik, 2000).

These volcano-hosted hydrothermal systems are accessible to sampling at surface manifestations (springs, pools) or where tapped by wells. Because volcanic groundwater are so intimately related to processes taking place within the volcano engine, their chemical composition has long been used to monitor volcanic activity state, and to possibly identify hydrogeochemical precursors in the run-up to eruption (Martini,

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1986; Martini et al., 1991; Shevenell and Goff, 1993; Bonfanti et al., 1996a, 1996b; Chiodini et al., 1996; Cairo et al., 1998, 1999, 2004; Delmelle et al., 1998; Sorey et al., 1998; Capasso et al., 1999; Valentino et al., 1999; Brombach et al., 2000; Goff et al., 2000; Lewicki et al., 2000; Varekamp et al., 2001; Tassi et al., 2003; Federico et al., 2004, 2023; Valentino and Stanzione, 2004; Evans et al., 2004; Lowenstern and Hurwitz, 2008; Rizzo et al., 2009, 2015; Hemmings et al., 2015; Jasim et al., 2015, 2018; Jasim, 2016; McCleskey et al., 2016).

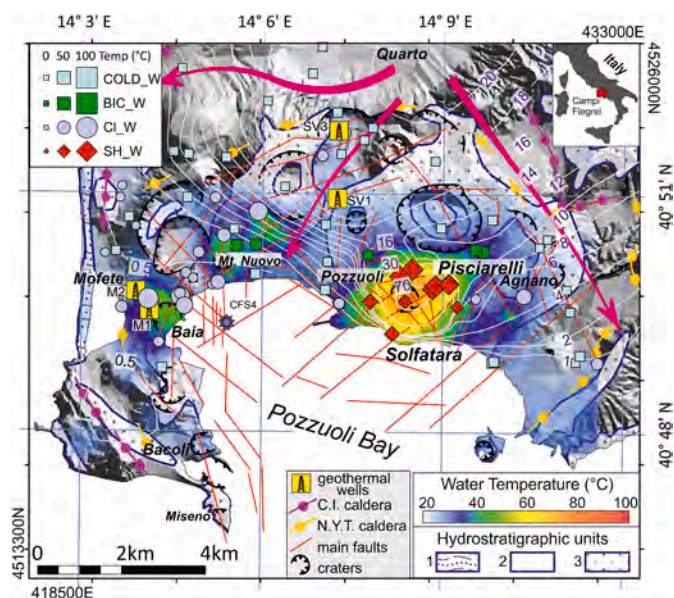
The composition of volcanic groundwater is primarily controlled by the rates and mechanisms of gas-water-rock interaction within the aquifer (Giggenbach, 1988; Stimac et al., 2015). These in turn depend upon a variety of physical and chemical factors, which vary in both space (at the scale of the aquifer) and time. Spatial-temporal heterogeneities combine to produce very diverse environments of water-gas-rock interaction, causing the remarkable diversity of groundwater chemistry seen at volcanoes.

The Campi Flegrei caldera (CFC, Orsi et al., 2022 and references therein), in the densely inhabited metropolitan area of Naples (southern Italy), hosts a powerful hydrothermal system both in its submerged (the bay of Pozzuoli) and onshore sectors (Chiodini et al., 2022), with a number of especially vigorous surface manifestations (fumaroles, steaming and degassing soils/ground, and hot waters) concentrated within (and in proximity of) the Solfatara crater (Marini et al., 2022) (Fig. 1). The caldera is characterized by the “bradyseism” phenomena; literally, the term “bradyseism” derives from the Greek idiom and means “slow movement”. It is widely used in the literature to identify the ground deformation occurring in the area of Pozzuoli village in the CFC, consisting in alternating phases of slow subsidence with generally more rapid uplift phases accompanied by low-magnitude earthquakes. The caldera entered a phase of unrest in the 1940s (Scarpa et al., 2022), with a further intensification in ground uplift and seismicity that took place during three bradyseismic crises in 1970–1972 (Corrado et al., 1977), 1982–1984 (Barberi et al., 1984) and 2005–present (Chiodini et al., 2016) motivated extensive research on hydrothermal fluid composition and flux (Cioni et al., 1984; Chiodini et al., 2001, 2003, 2016; Cairo et al., 2007, 2014). According to Cairo et al. (2007, 2014), the hydrothermal system is fed by a mixture of hot magmatic fluids (delivered by mafic magma stored at depth) and vapor generated by high temperature (~360 °C) vaporization of hydrothermal liquids of meteoric origin. This mixing zone is inferred to be located at the base of the hydrothermal system (at about 2 km depth), and to be overlain by a vapor-dominated plume centered underneath the Solfatara (Chiodini et al., 2022). Physical simulations (Chiodini et al., 2003, 2012, 2016) suggest that repeated pulses of magmatic gas injections into the hydrothermal system, caused by magma degassing episodes, are the likely driver of the unrest, and that these degassing episodes have increased in frequency (Chiodini et al., 2021, 2022) and injected mass of magmatic gases (Chiodini et al., 2016, 2021; Cardellini et al., 2017) during accelerating unrest since 2012.

As noted above, the chemical composition of groundwater is, at least in principle, an invaluable source of information to track episodes of escalating magmatic gas transport into the shallow hydrothermal system. However, no systematic characterization of groundwater chemistry has been attempted at CFC since acceleration of the unrest in 2012. Here, we report on the results of an extensive hydrogeochemical survey carried out in 2013–2014 to geochemically and isotopically (He, C, H and O isotopes) characterize the CFC groundwater system. Our aim here is to identify the main processes that control groundwater chemistry, and to derive hints into the source and fate of the released fluids:

## 2. The Campi Flegrei caldera (CFC)

The CFC is a long-lived resurgent caldera covering a large part of the coastal area west of Naples, Italy (Orsi et al., 1996, 2022). The present structure, comprising a 12 km wide caldera with other minor depressions, was largely determined by two main paroxysmal events, the



**Fig. 1.** Distribution of groundwater temperature based upon water samples collected in this work (sampling point locations shown), integrated with data from Aquater spa (1978), Aiuppa et al. (2006), Petrillo et al. (2013) and additional groundwater temperature measurements taken in the period from 2001 to 2018. Two main thermal clusters are present in the Solfatara-Pisciarelli and Baia Mofete areas. Contour lines are the water table surface and blue numbers indicate the piezometric level in meter a.s.l. (Petrillo et al., 2013; De Vita et al., 2018). Magenta arrows indicate aquifer main preferential drainage. The elevated water table in Solfatara area is fed by fumarolic condensates. Red diamonds, steam-heated groundwater (SH\_W); light blue squares, meteoric groundwater (COLD\_W); green squares, bicarbonate-dominated thermal waters (BIC\_W); grey circles, chlorine-dominated waters (CL\_W); purple star, submarine vents from the Fumose area (samples CFS4). Groundwater symbol dimensions are proportional to the water temperature. Geothermal wells: Mofete1 (M1), Mofete2 (M2), San Vito1 (SV1), San Vito3 (SV3). Campanian Ignimbrite caldera (C.I.); Neapolitan yellow tuff caldera (N.Y.T.); main faults and craters are modified after Selva et al. (2012) and Di Napoli et al. (2016). Hydrostratigraphic units: 1) alluvial-coastal complex formed by incoherent clastic deposits comprising all grain size classes, but with prevailing sandy terms. These deposits constitute heterogeneous and anisotropic porous aquifers. Groundwater flow can have hydraulic interchanges with freshwater bodies and/or with groundwater of the adjoining hydrogeological units; 2) ash-fall pyroclastic complex formed by incoherent deposits comprising lapilli and ashes, which, depending on different grain size classes, constitute heterogeneous and anisotropic porous aquifers with a generally low transmissivity; 3) ash-flow pyroclastic complex formed by ignimbrite deposits, from welded to scarcely welded, constituting anisotropic porous and fractured aquifers, generally characterized locally by a moderate transmissivity. Map of temperature was produced using the Sequential Gaussian Simulation algorithm (Deutsch and Journel, 1998). Coordinates are reported as geographic latitude and longitude and metric referring to the UTM projection (33 T zone), WGS84 datum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Campanian Ignimbrite (39 ka BP) and Neapolitan Yellow Tuff (14 ka BP) eruptions (De Vivo et al., 1989; Orsi et al., 1992; Blockley et al., 2008). Over the last 14 ka, volcanic activity has occurred mainly within the caldera, commonly focused along its rim and regional faults (di Vito et al., 1999). After the last eruptive event (the Monte Nuovo eruption in 1538 A.D.; Di Vito et al., 2016), periodic episodes of unrest have occurred (Scarpa et al., 2022). Since the 1940s, CFC has been showing clear signs of potential reawakening, as revealed by recurrent episodes of ground uplift, shallow seismicity, and a visible increase in hydrothermal degassing (Del Gaudio et al., 2010; D’Auria et al., 2011; Chiodini et al., 2015). Two main uplift phases were recorded in 1970–1972 and in 1982–1984. In both cases, the deformation was confined within a radius

of 6 km, with maximum values registered at the center of the caldera of about 1.70 m and 1.80 m, respectively (Scarpa et al., 2022). The 1982–1984 bradyseism (Barberi et al., 1984) was followed by ~20 years of subsidence that terminated in November 2004, when ground uplift resumed, totaling about 1.3 m by the time of writing, and being accompanied by intense seismicity since 2018 (D'Auria et al., 2015; Chiodini et al., 2016; Bevilacqua et al., 2022; Kilburn et al., 2023; Giacomuzzi et al., 2024).

### 3. Hydrogeological background

The Campi Flegrei hydrothermal system has extensively been studied in the attempt to understand underground fluid circulation (Dall'Aglio et al., 1972; Celico et al., 1991; Rolandi and Stanzione, 1993; Tedesco et al., 1996) and the relations between bradyseismic events and groundwater chemistry (Ghiara and Stanzione, 1988; Martini et al., 1991; Celico et al., 1992; Tedesco, 1994).

The hydrogeological structure of the CFC is complicated by the presence of several overlapping lithotypes (e.g., tuffs, lava and sedimentary rocks) of variable thickness, grain-size distribution, porosity and permeability. The ultimate effect of this complex stratigraphy is the occurrence of different porous (unwelded pyroclastic deposits) and fractured (welded pyroclastic deposits and lavas) aquifers at shallow depths (Celico et al., 1987, 1991, 1992; Rosi and Sbrana, 1987; Allocca et al., 2018; Stellato et al., 2020; De Vita et al., 2018). Shallow groundwater circulation in the western and central sectors of the caldera defines an area with high piezometric levels, approximately 22 m a.s.l. in the Quarto area and ~70 m a.s.l. centered at the Solfatara area (Fig. 1) (e.g., Celico et al., 1991; De Vita et al., 2018), probably associated with deep fluid upwelling (Bruno et al., 2007). At the regional scale, a pseudo-radial groundwater flow pattern is defined by groundwater circulation towards the coastline in the southern, southeastern and western sectors, and towards the Campanian Plain aquifer in the northern sector (Celico et al., 1992; De Vita et al., 2018).

The bell shaped geometry of the water table in the Solfatara-Pisciarelli area (Fig. 1, Petrillo et al., 2013) is interpreted to be caused by the supply of steam condensates impacting the circulation and the chemical composition of groundwater in this area and surroundings.

Geothermal exploration wells drilled to about 3 km depth in the Mofete and San Vito areas (Fig. 1) have shed light into the deeper hydrothermal fluid circulation pathways (Guglielminetti, 1986; Rosi and Sbrana, 1987; De Vivo et al., 1989; Caprarelli et al., 1997), revealing the existence of a multi-reservoir geothermal system at depth (in the 550–2700 m depth range), characterized by high fluid salinities and temperatures (250–390 °C), and very diverse fluid origins (from primarily seawater-derived at <2000 m depth, to meteoric-magmatic in origin at >2000 m depth). These deep hot brines can locally rise through faults and fractures to mix with shallow groundwater (Aiuppa et al., 2006). These volcano-tectonic discontinuities also locally favor ascent and mixing between groundwater, deep and CO<sub>2</sub>-rich mineralized fluids, and seawater.

### 4. Sampling and analytical methodologies

We report here on the composition of 114 water samples collected at CFC during May 2013 to March 2014. Samples are spatially distributed over an area of about 100 km<sup>2</sup> (Fig. 1). Values of pH, Eh, Electrical Conductivity (EC) and total alkalinity were determined directly in the field during sampling. Alkalinity was measured by acid titration with HCl 0.1 N on 100 ml of sample using methyl-orange as indicator. Water samples for chemical analyses were filtered with 0.45 µm filters and collected in 30 ml high-density polyethylene (HDPE) bottles. One aliquot was acidified with HCl 1:1 for the determination of cations. Samples were analyzed at the laboratory of fluid geochemistry at the INGV-Osservatorio Vesuviano, Naples. Major ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were determined by ion chromatography

using a Dionex ICS3000 system. Dissolved gases (CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>, He) in water were analyzed following a modified method based on Chiodini (1996) and Caliro et al. (2008). Samples were collected in pre-evacuated ~200 ml glass vials equipped with a Teflon stopcock fixed with a rubber O-ring. In the field, the vial was filled with a volume of water, V<sub>liq</sub> of about 2/3 of the total vial volume, V<sub>tot</sub>. The gas phase separated in the headspace of the vial, of volume V<sub>gas</sub> = V<sub>tot</sub> - V<sub>liq</sub>, was analyzed by a gas-chromatograph (HP 6890 N) through a unique injection on two analytical channels equipped with capillary columns (Molecular Sieve 5 Å 30 m × 0.53 mm × 50 µm and PLOT Q 30 m × 0.53 mm × 20 µm) and TCD detectors, using He as carrier gas on both channels. The partial pressure of each gas species (CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>) was determined referring to pure components at different pressures. Helium partial pressure in the head space of the vials was determined, on a second injection, by a leak detector (Alcatel ASM 142 - detection limit 0.00015 mbar). Based on partial pressure (P<sub>i</sub>), the numbers of moles n<sub>i,g</sub> of each gas species contained in V<sub>gas</sub> + V<sub>inj</sub> (where V<sub>inj</sub> is the measured volume of the gas injection line) are calculated through the ideal gas law. After computing the partial pressures in the headspace of the vials (p<sub>i,g</sub> = (P<sub>i</sub> \* (V<sub>gas</sub> + V<sub>inj</sub>)) / V<sub>gas</sub>), the number of moles of each gas species n<sub>i,l</sub> remaining in the liquid are calculated by means of the Henry's law (constants from Wilhelm et al., 1977), assuming that the gas phase separated in the headspace of the vial is in equilibrium with the liquid at laboratory temperature. The sum n<sub>i,g</sub> + n<sub>i,l</sub> gives the total moles of each gas species in the water sample. The effect of salinity on gas solubility was not taken into account, as salinities of the examined solutions are relatively low.

For the determination of δ<sup>13</sup>C of Total Dissolved Inorganic Carbon (TDIC), carbon species were precipitated in the field as SrCO<sub>3</sub> by adding SrCl<sub>2</sub> and NaOH as solid reactants directly in the sampling bottle. Carbonate precipitates were filtered and washed with CO<sub>2</sub>-free distilled water under nitrogen atmosphere. Carbon isotope analyses were performed using a Finnigan Delta plus XP continuous flow mass spectrometer coupled with a Gasbench II device (analytical error δ<sup>13</sup>C ± 0.06 ‰; data reported vs. V-PDB, Vienna Pee Dee Belemnite).

The oxygen and hydrogen isotopic composition of the collected waters was estimated by a near infrared laser analyzer (Picarro L2130i) using the wavelength-scanned cavity ring down spectroscopy technique (analytical errors: δ<sup>2</sup>H ± 0.5 ‰, δ<sup>18</sup>O ± 0.08 ‰; data reported vs. Vienna Standard Mean Ocean Water, V-SMOW).

The isotopic composition of He (as <sup>3</sup>He/<sup>4</sup>He) of the dissolved gas sample was determined at INGV-Sezione di Palermo, using a Helix SFT-GVI mass spectrometer for the isotopic measurements of helium and a Helix MC-Plus Thermo for <sup>20</sup>Ne, according to the method proposed by Inguaggiato and Rizzo (2004). Data are reported as R/R<sub>a</sub> values (R<sub>a</sub> is the He isotopic ratio in the atmosphere, as 1.39 × 10<sup>-6</sup>; Ozima and Podosek, 2002), corrected for the atmospheric contamination using the sample <sup>4</sup>He/<sup>20</sup>Ne ratio (Sano and Wakita, 1985).

The locations of sampling sites are reported in the map of Fig. 1, while the chemical and isotopic compositions of thermal waters are listed in Table S1.

## 5. Results

### 5.1. Physico-chemical parameters and major element composition

The sampled groundwaters are very diverse in terms of their physical parameters and chemistry of major ions (Table S1). Outlet temperature varies between 10.1 and 85.8 °C, pH from 1.54 to 8.9, electrical conductivity from 397 to 37,100 µS/cm, and total dissolved solids (TDS) from 93 to 34,200 mg/l (Table S1). About 60 % of the samples have pH less than 7, suggesting a pervasive interaction with volcanic/hydrothermal fluids rich in acidic volatiles (CO<sub>2</sub> and H<sub>2</sub>S are major acidic species in the Solfatara fumaroles; Caliro et al., 2007). This is consistent with the widespread temperature anomaly that, while extending to the entire aquifer system, is particularly well visible in the Solfatara-

Pisciarelli area (Fig. 1). There, groundwater outlet temperatures of  $>60\text{ }^{\circ}\text{C}$  are primary evidence for heating caused by the addition of hot fluids into the shallow aquifer. Electrical conductivity and TDS are broadly correlated with outlet temperature (Fig. 2 and Table S1). Cold groundwater ( $T < 25\text{ }^{\circ}\text{C}$ ) of likely meteoric origin typically contains less dissolved salts ( $< 1500\text{ mg/l}$ ) than thermal waters, in which water-rock interaction is enhanced by higher temperatures, more intense rock leaching, and more powerful interaction with deeply sourced volcanic/hydrothermal fluids.

Diversity in groundwater chemistry is also illustrated in the Piper's diagram of Fig. 3, in which, as previously found (Valentino et al., 1999; Valentino and Stanzione, 2003, 2004; Aiuppa et al., 2006), three main water types can be identified: (1) bicarbonate-dominated groundwater, further separated into cold groundwater (COLD\_W) and bicarbonate thermal waters (BIC\_W) based on their temperatures and TDS (Fig. 2); (2) higher temperature (Fig. 2) chlorine-dominated groundwater (Cl\_W); and (3) sulphate-dominated groundwater that, owing to their high temperatures (Fig. 2) and close proximity to the Solfatara-Pisciarelli fumarolic field (Fig. 1), are interpreted as steam-heated groundwater (SH\_W; sensu Giggenbach, 1988) derived by the condensation of high-temperature,  $\text{H}_2\text{S}$ -rich hydrothermal steam (Aiuppa et al., 2006).

COLD\_W are predominantly found along the peripheries of the caldera (Fig. 1) and, in addition to having low TDS ( $< 1500\text{ mg/l}$ ) and temperatures ( $< 25\text{ }^{\circ}\text{C}$ ), are poor in alkalis (Fig. 4a, b) and have calcium as the main cation (Fig. 2). They are hence good proxies for the local meteoric recharge (Fig. 4). Cl\_W, in contrast, are the most saline waters found at CFC (Fig. 2) and, being Na-K-rich, approach the composition of local seawater and the deep reservoir brines tapped by the Mofete geothermal wells (Fig. 4 a, b). Water samples (samples CFS4) collected in the submarine vents of the Fumose area (Di Napoli et al., 2016) exhibit similar alkalis-chlorine-rich compositions (Figs. 3–4). BIC\_W have compositions intermediate between COLD\_W and Cl\_W (Fig. 4). Finally, SH\_W are especially chlorine- and alkali-poor, confirming their mineralization is not controlled by mixing with either seawater or hydrothermal brines (as for the Cl\_W), but rather by condensation of  $\text{H}_2\text{S}$ -rich fumarolic steam, followed by pervasive leaching of host rocks.

## 5.2. Oxygen and hydrogen isotopic composition

In previous work on oxygen and hydrogen isotopic compositions (Baldi et al., 1975; Valentino et al., 1999; Bolognesi et al., 1986), the CFC thermal waters have been interpreted as binary mixtures of local

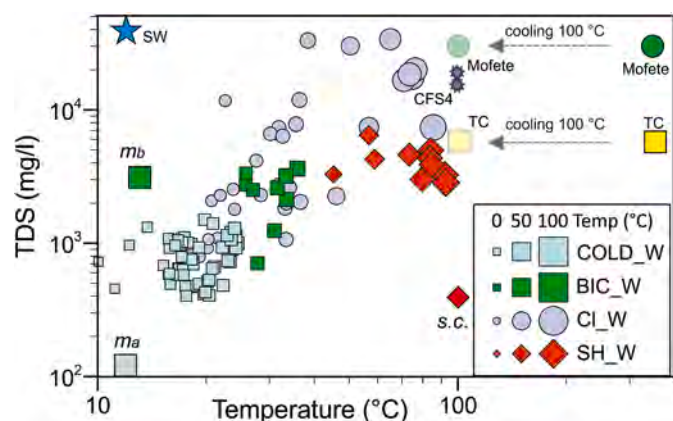


Fig. 2. Temperatures vs. total dissolved solids (TDS) scatter plot. Different symbols are used for the different water types, dimension of the symbols is proportional to the water temperature. Seawater and others endmembers (SW = seawater;  $m_a$  = meteoric low salinity;  $m_b$  = meteoric bicarbonate; sc = steam condensate; Mofete = saline hydrothermal component; TC = low salinity hydrothermal component) are reported for comparison, see text for more details.

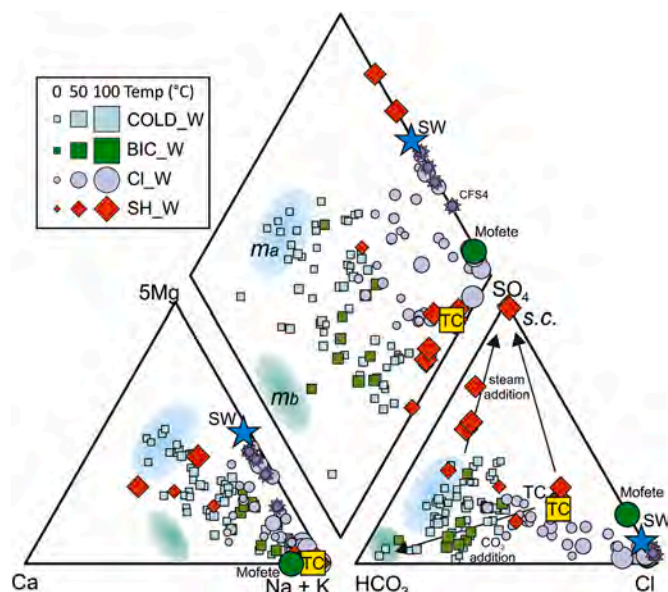


Fig. 3. Piper (1944) diagram. Symbols as in Fig. 2.

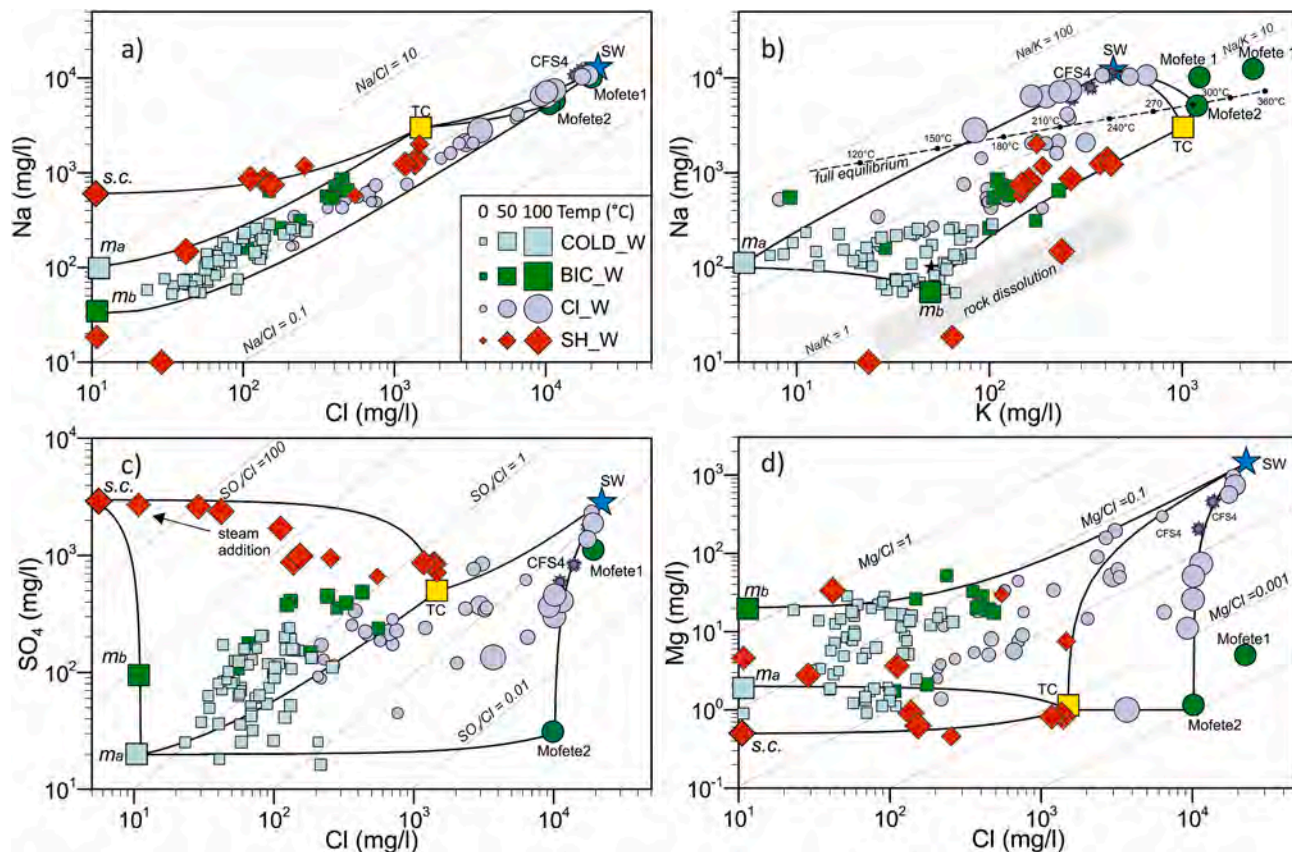
meteoric water ( $\delta^{18}\text{O}$  -6.7 to  $-8\text{ }^{\circ}\text{‰}$  and  $\delta^2\text{H}$  -33 to  $-42\text{ }^{\circ}\text{‰}$ ) and hot deep hydrothermal reservoir waters of marine origin ( $\delta^{18}\text{O}$  + 1.2  $\text{‰}$ ,  $\delta^2\text{H}$  + 12  $\text{‰}$ ). The recharge area of the meteoric component has been inferred to correspond to the carbonate massifs bordering the caldera, at a mean elevation of 370 m (Baldi et al., 1975).

Figure 5 illustrates our O and H isotopic results. In addition to the groundwater samples, we also plot the isotopic compositions of bulk steam condensates from the Solfatara fumaroles (Cairo et al., 2007), the calculated isotopic composition of liquids at equilibrium (at  $100\text{ }^{\circ}\text{C}$ ) with the same Solfatara steam samples (we use liquid-vapor fractionation factors of  $1000\ln\alpha_{(l-v)}(^{18}\text{O}) = 5.08$  and  $1000\ln\alpha_{(l-v)}(^2\text{H}) = 27.9$ , respectively, Horita and Wesolowski, 1994), the isotopic composition of local seawater, and the local meteoric water-line (Cairo et al., 1998).

Our CFC groundwaters exhibit an impressive isotopic variability, with  $\delta\text{D}$  and  $\delta^{18}\text{O}$  compositions ranging from  $-46$  to  $+22.3\text{ }^{\circ}\text{‰}$  and from  $-7.7$  to  $+6.8\text{ }^{\circ}\text{‰}$  versus V-SMOW, respectively.  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  compositions are broadly positively correlated (Fig. 5a), identifying a linear trend with a slope of  $\sim 5$ , well below that of the meteoric water line. COLD\_W and BIC\_W plot above (or close to) the meteoric water line, confirming their meteoric derivation. In contrast, Cl\_W, SH\_W, and submarine vents (CFS samples) depart from the meteoric water line and point towards one (or more) isotopically heavy end-member component (s), lying somewhere between local seawater and the composition of the Mofete 1 hydrothermal brines (Fig. 5a). The most extreme isotopic compositions are observed for the Solfatara and Pisciarelli mud pools, whose extremely heavy  $\delta^2\text{H}$  ( $> +10\text{ }^{\circ}\text{‰}$ ) and  $\delta^{18}\text{O}$  ( $> +4\text{ }^{\circ}\text{‰}$ ) compositions suggest an input steam condensate and further non-equilibrium isotopic fractionation during boiling/evaporation at surface conditions (Giggenbach and Stewart, 1982). These processes of input of  $^2\text{H}$  and  $\delta^{18}\text{O}$  rich and Cl poor fumarolic steam condensate and surface boiling are depicted in Fig. 5b.

## 5.3. Dissolved gases

All groundwater samples contain gas species in dissolved form (Table S1).  $\text{CO}_2$  is the dominant dissolved gas species in most samples (range, 0.005–33.8 mmol/l), followed by  $\text{N}_2$  (0.04–1.12 mmol/l),  $\text{O}_2$  (from b.d.l. to 0.4 mmol/l), and Ar (0.0006–0.03 mmol/l).  $\text{CH}_4$  is observed at detectable levels (0.0002–0.22 mmol/l) in only 40 out of 112 samples, while He is observed at trace levels ( $2 \times 10^{-6}$  - 0.0001 mmol/l) in all samples. Owing to the complex behavior of carbon in



**Fig. 4.** Log-log scatter plots of major elements: a) Na vs. Cl; b) Na vs. K; c)  $\text{SO}_4$  vs. Cl; d) Mg vs. Cl, of CF. Chemical composition of groundwater can be accounted for by mixing of different endmembers (see text), mixing lines are reported as black lines in the panels. In addition, panel b) reports the full equilibrium composition (Giggenbach, 1988), drawn assuming that Mg activity is controlled by the equilibrium with Mg-Chlorite in the temperature range of interest (Giggenbach et al., 1983), calculations were done by means of PHREEQC code (Parkhurst and Appelo, 1999). Note the relatively high Na and K concentrations of the “fully equilibrated” water.

aqueous solutions (see discussion), we use Total Dissolved Inorganic Carbon (instead of the  $\text{CO}_2$  concentration) as a better proxy to fully characterize the carbonate system.

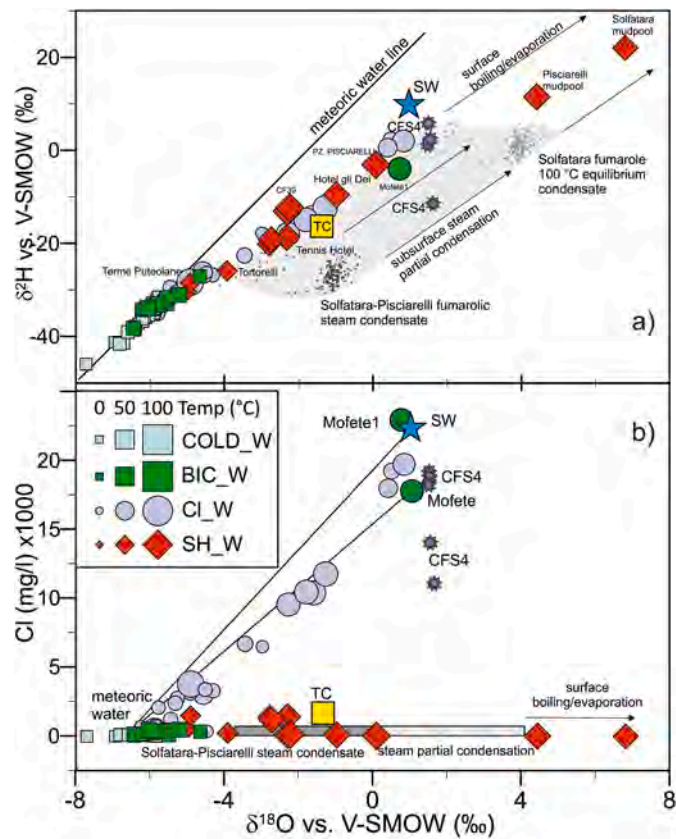
Carbon concentration (TDIC) and  $\text{N}_2$  are broadly negative correlated (Fig. 6a), implying diverse sources. High TDIC concentrations are in general characterized by high  $\text{pCO}_2$  values and are associated with low  $\text{N}_2$  and Ar concentrations (Table S1). This behavior suggests that the addition of a deep  $\text{CO}_2$  rich gas phase leads to an increase in the total pressure of dissolved gases, and causes degassing upon ascent/decompression, indicating a barometric control on the composition of the dissolved gases. The most  $\text{N}_2$ -rich samples are the meteoric-derived (Fig. 5) COLD\_W, suggesting atmospheric derivation of this gas. This is corroborated by the positive correlation between  $\text{N}_2$  and Ar (Fig. 6b), with most COLD\_W exhibiting  $\text{N}_2/\text{Ar}$  of  $\sim 40$ , close to that of air-saturated water at 0–20 °C and 0–1200 m (the supposed meteoric water infiltration temperature and elevation, based on the height of carbonate massifs boarding the Campanian Plain). Samples with  $\text{N}_2/\text{Ar}$  ratios of  $\sim 83$  reflect air contamination upon (or prior to) sampling. Oxygen, the second most abundant component in air, is high in many  $\text{N}_2$ -rich groundwaters (Table S1), but the weak  $\text{N}_2$ - $\text{O}_2$  correlation (not shown) reflects its non-conservative behavior upon infiltration and groundwater discharge ( $\text{O}_2$  is typically consumed by redox reactions in aquifers; at CFC, this is testified by recurrent reducing redox conditions, with measured redox potentials ( $E_{\text{H}}$ ) as a low as  $-241$  mV). Thermal waters (BIC\_W, CI\_W, and SH\_W) are to a variable extent depleted in air components and enriched in  $\text{CO}_2$ , with the most  $\text{CO}_2$ -rich samples corresponding to BIC\_W. In the thermal waters,  $\text{CO}_2$  levels are well in excess of those characteristic of air saturated groundwater, requiring an

additional, non-atmospheric source.

#### 5.4. He and C isotopes

Helium has very contrasting  $^3\text{He}/^4\text{He}$  signatures, having  $\text{R}/\text{Ra} = 1$  in air,  $\text{R}/\text{Ra} \sim 0.02$  in the continental crust (Ozima and Podosek, 2002), and in the Earth’s mantle  $\text{R}/\text{Ra} > 1$  (with MORB range at  $8 \pm 1$  Ra; Graham, 2002). Thus, this ratio is a very useful tracer to resolve atmospheric vs. endogenous (magmatic, mantle, or crustal) sources of fluids in volcanic groundwater (Sano and Fischer, 2013). Dissolved He in the CFc groundwater samples is isotopically heterogeneous, ranging from 0.089 to 2.73  $\text{R}/\text{Ra}$  and a  $\text{Ne}/\text{He}$  from 0.17 to 13.1, with the highest  $\text{R}/\text{Ra}$  values approaching the isotopic compositions of the Solfatara fumaroles.

Figure 7 plots the He isotope compositions of our groundwater samples vs. (a) the  $\text{Ne}/\text{He}$  ratio and (b) the  $\text{N}_2/\text{He}$  ratio. These chemical ratios between inert/unreactive components are suitably combined with He isotopes because they are orders of magnitude higher in air than in the crust/mantle (Fig. 7). We find a broad negative correlation between  $\text{R}/\text{Ra}$  and  $\text{Ne}/\text{He}$ - $\text{N}_2/\text{He}$  ratios (Fig. 7), indicating that the data variability is predominantly controlled by mixing between an atmospheric component (air, and/or air-saturated groundwater) and a Solfatara-like hydrothermal gas. However, a number of groundwater samples have  $\text{R}/\text{Ra}$  composition well below 1, and trend towards a possible crustal endmember characterized by  $\text{R}/\text{Ra} \sim 0.02$ , a  $\text{Ne}/\text{He}$  ratio 0.001 and  $\text{N}_2/\text{He}$  ratio of 1.000, compatible with a radiogenic crustal source (Sano and Wakita, 1985). These endmembers are estimated by fitting samples compositions with simple mixing models as depicted in Fig. 7. In



**Fig. 5.** Chemical-isotopic diagrams of CF groundwater: a)  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  and b)  $\delta^{18}\text{O}$  vs. Cl. Composition of steam discharged by the Solfatara vents, of seawater, of submarine thermal water CFS4 (Di Napoli et al., 2016), the meteoric water-line (Cairo et al., 1998) and the composition of the equilibrium liquid phase condensed from steam of Solfatara vents at 100 °C are also reported.

particular, most of the samples indicate that all the three endmembers are concurrently involved in defining the dissolved gas compositions. The fractions of each endmember can be derived from the following equations (modified from Sano and Wakita, 1985):

$$\left(\frac{^3\text{He}/^4\text{He}}{\text{He}}\right) = \left(\frac{^3\text{He}/^4\text{He}}{\text{He}}\right)_a \times fA + \left(\frac{^3\text{He}/^4\text{He}}{\text{He}}\right)_h \times fH + \left(\frac{^3\text{He}/^4\text{He}}{\text{He}}\right)_r \times fR \quad (1)$$

$$\left(\frac{^{20}\text{Ne}/^4\text{He}}{\text{He}}\right) = \left(\frac{^{20}\text{Ne}/^4\text{He}}{\text{He}}\right)_a \times fA + \left(\frac{^{20}\text{Ne}/^4\text{He}}{\text{He}}\right)_h \times fH + \left(\frac{^{20}\text{Ne}/^4\text{He}}{\text{He}}\right)_r \times fR \quad (2)$$

$$1 = fA + fH + fR \quad (3)$$

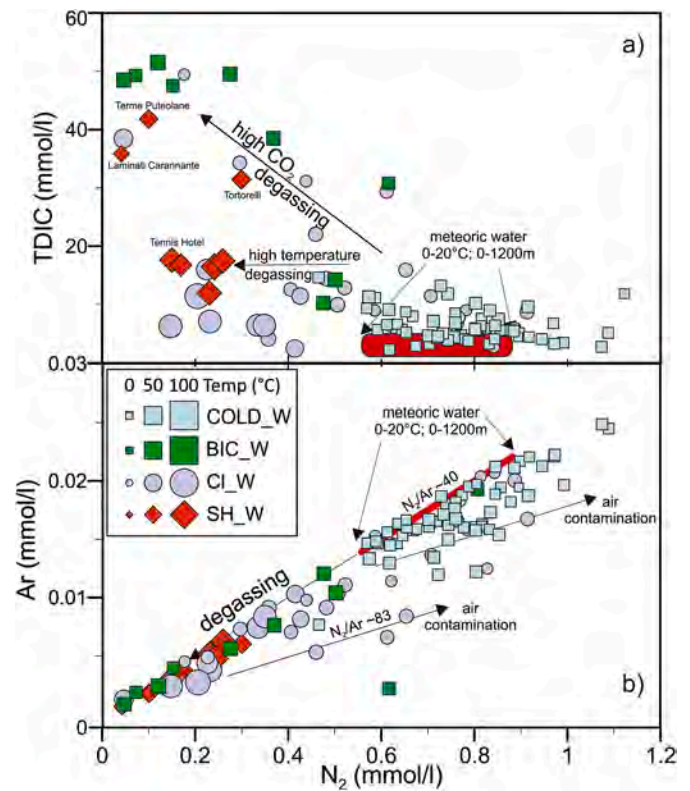
where the subscripts *a*, *h*, and *r* refer to the asw, hydrothermal and radiogenic (crustal) endmembers, respectively. The computed correspondent fractions *fA*, *fH* and *fR* are reported in Table S1.

A similar approach can be applied to derive endmember fractions by considering nitrogen concentrations. Accordingly, eqs. 1 and 3 remain the same while eq. 2 can be written as:

$$\left(\frac{\text{N}_2/^4\text{He}}{\text{He}}\right) = \left(\frac{\text{N}_2/^4\text{He}}{\text{He}}\right)_a \times fA + \left(\frac{\text{N}_2/^4\text{He}}{\text{He}}\right)_h \times fH + \left(\frac{\text{N}_2/^4\text{He}}{\text{He}}\right)_r \times fR \quad (4)$$

Figure 7a and b also report the mixing lines computed for fractions of hydrothermal component (*fH*) of 10 %, 50 % and 90 %.

The carbon isotope composition ( $\delta^{13}\text{C}$ ) of Total Dissolved Inorganic Carbon (TDIC) varies from  $-17.1$  ‰ to  $+2.34$  ‰ (Table S1). The meteoric-derived COLD\_W exhibits the lightest (most negative)  $\delta^{13}\text{C}$  values ( $-17.3$  to  $-5.1$  ‰), reflecting a primary biogenic origin of TDIC (2.2–14.5 mmol/l) (Fig. 8). Thermal waters (BIC\_W, CI\_W, and SH\_W)



**Fig. 6.** Dissolved gases in CF groundwater: a)  $\text{N}_2$  vs. TDIC and b)  $\text{N}_2$  vs. Ar. Depletion in atmospheric components is accompanied by an increase of TDIC ( $\text{CO}_2$ ) and/or induced by the increased temperature of groundwater. The addition of a  $\text{CO}_2$  rich gas phase leads to an increase in the total pressure of dissolved gases, and causes degassing upon ascent/decompression, suggesting barometric control on the composition of the dissolved gases.

are increasingly enriched in an isotopically heavy carbon component. For reference, the characteristic  $\delta^{13}\text{C}$  composition of the Solfatara fumaroles is  $-1.3 \pm 0.4$  ‰ (Cairo et al., 2014).

## 6. Discussion

In regions of active volcanism, groundwater stands at the interface between the shallow meteoric system and the underlying magmatic-hydrothermal system. As such, groundwater composition reflects a dynamic balance resulting from fluid contributions from both surface (atmosphere/biosphere/seawater) and deeper (crustal rocks, magmas, and their mantle sources) environments (Jasim et al., 2018). The complex interactions that result cause volcanic groundwater to vary widely in both space (at the scale of a given volcanic aquifer) and time, a fact that can potentially be exploited to monitor volcanic activity state when/if the volcano becomes restless (e.g., Cronan et al., 1997). For volcanic groundwaters to be useful for volcano monitoring, however, a thorough understanding of the processes that control their chemistry is required. This is today especially relevant at CFC, in view of the ongoing deformation/seismic/degassing unrest beginning in the early 2000s (Chiodini et al., 2003, 2016, 2021) and that continues at an accelerating rate (Kilburn et al., 2017, 2023; Bevilacqua et al., 2022) at the time of this writing. Here we use the results of our comprehensive 2013–2014 hydrogeochemical survey, the first since the bradyseismic crisis, to analyze the key processes controlling groundwater chemistry at CFC.

### 6.1. Steam condensation

Perhaps the most striking aspect of our dataset is the prominent groundwater temperature anomaly in the Solfatara-Pisciarelli district

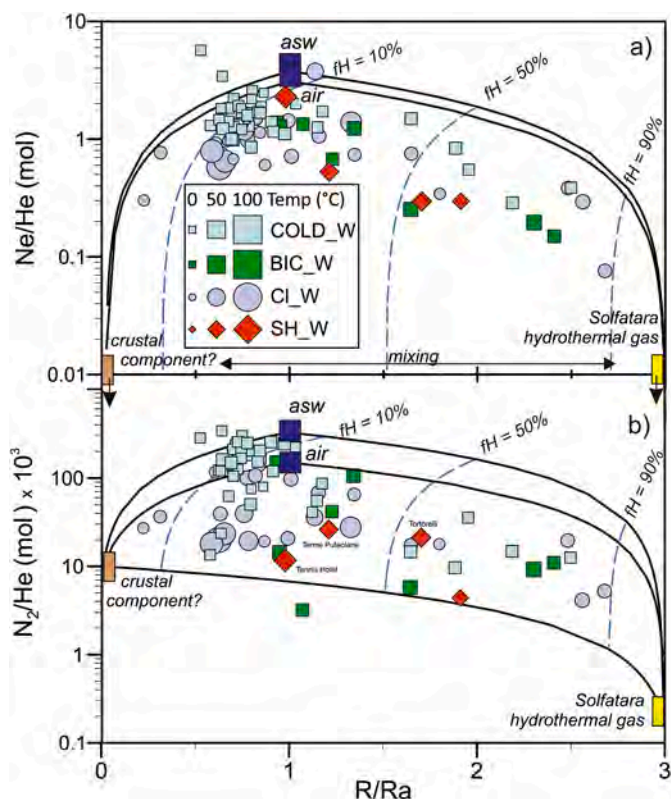


Fig. 7. He isotope composition ( $R/Ra$ ) of CFC groundwater samples, plotted versus (a)  $Ne/He$  and (b)  $N_2/He$  ratios. The mixing lines between different end-members are shown, along with the mixing lines computed for 10 %, 50 % and 90 % fractions of the hydrothermal components ( $fH$ ) (see text).

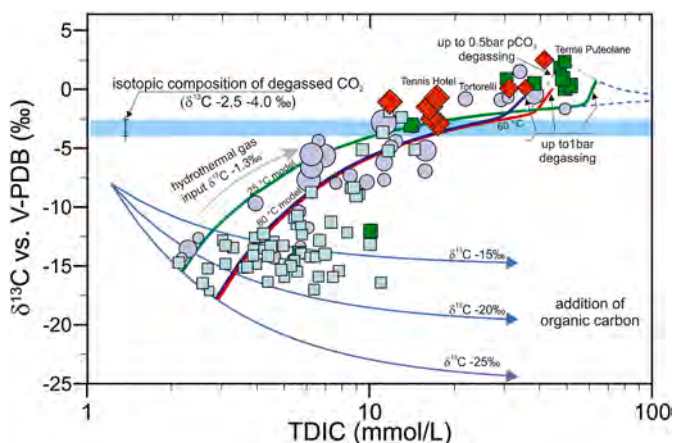


Fig. 8.  $\delta^{13}C_{TDIC}$  vs. TDIC scatter plot of CFC groundwater. Samples exhibit a general trend from low TDIC and  $^{13}C$ -depleted compositions towards high TDIC and more positive  $\delta^{13}C$  compositions. The figure also shows the model evolution of groundwater as calculated by numerical simulations: blue lines, obtained by adding to a meteoric water (with a TDIC of  $\sim 1$  mmol/L and  $\delta^{13}C$  of  $-8$  ‰) a  $CO_2$  with biologic signature from  $\delta^{13}C$   $-25$  ‰ to  $-15$  ‰. The input of biologic carbon during the infiltration is evident for the bicarbonate cold water. Green, red and purple lines: starting from the results of the previous models, three simulations are carried out at different temperatures (25–60–80 °C) by adding 0.1 mol of a hydrothermal Solfatara-like gas phase in 100 steps, allowing the solution to degas at 1 bar of total gas pressure. Degassing lines at 0.5 bar of  $pCO_2$  are also reported as grey shaded lines.

(Fig. 1). The Solfatara crater is a maar-like, sub-hexagonal depression, bounded by steep faults, formed by repeated explosive (phreatic to phreatomagmatic) activity during the most recent epoch (epoch III) of volcanic activity at Campi Flegrei, at ca. 4200 yr B.P. (Isaia et al., 2015). With the adjacent Pisciarelli fumarolic system (Isaia et al., 2021), the Solfatara crater has historically been the largest hydrothermal manifestation in the CFC (Guidoboni and Ciuccarelli, 2011; Marini et al., 2022). Recently, hydrothermal activity from fumarolic vents, boiling mud pools, and steaming grounds/soils has significantly increased during the 1982–1984 (Orsi et al., 1999) and 2005–present (Chiodini et al., 2016, 2022) unrest. Because of this especially intense hydrothermal degassing activity, and based on geophysical (Isaia et al., 2015) and geochemical (Cairo et al., 2014) evidence, the Solfatara volcano has been interpreted (Chiodini et al., 2022) as the surface outflow zone of a vertically extended (from the base of the hydrothermal system at  $\sim 2$ –3 km depth to about 300–500 m depth) “gas plume”, formed by complete vaporization of hydrothermal brines by magma-sourced volatiles. Steam transported in this gas plume would condense in the near-surface (at 300–500 m depth), where electrical resistivity tomography (Byrdina et al., 2014; Troiano et al., 2014; Gresse et al., 2017) and audio-magneto-telluric (Siniscalchi et al., 2019) results indicate the presence of very conductive layer(s). According to Chiodini et al. (2001), condensation of not less than 3000 tons/day of steam would result in a heat energy transfer of about  $7.5 \cdot 10^{12}$  J/d. Steam condensates, supplied at a rate of about 40–50 L/s, are thought to feed the local aquifer, inducing the bell-shaped geometry of the water table in the Solfatara-Pisciarelli area (Fig. 9, Petrillo et al., 2013) and impacting the chemical and isotopic composition of groundwater in this area and surroundings. In light of the above, we interpret the temperature anomaly in the Solfatara-Pisciarelli district (Figs. 1, 9) to be (primarily) caused by heat generated by this steam condensation process.

Chemically, hydrothermal steam condensation is known to generate  $SO_4$ -dominated steam-heated groundwater, in which dissolved sulphate is produced by aqueous-phase oxidation of hydrothermal  $H_2S$  (Giggenbach, 1988). At CFC, the clustering of SH\_W groundwater in the Solfatara-Pisciarelli area, with high  $SO_4/Cl$  ratios (Fig. 10a), supports the prominent role of steam condensation in this area.

Steam condensation in the shallow aquifer is additionally strongly supported by O–H isotopic results (Fig. 5). Simple mixing between (i)

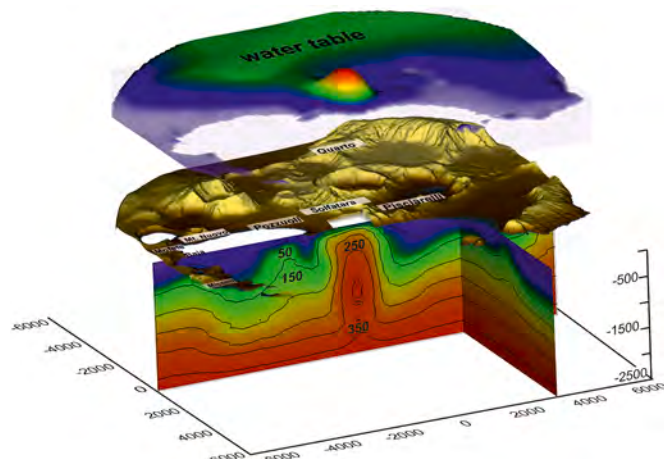
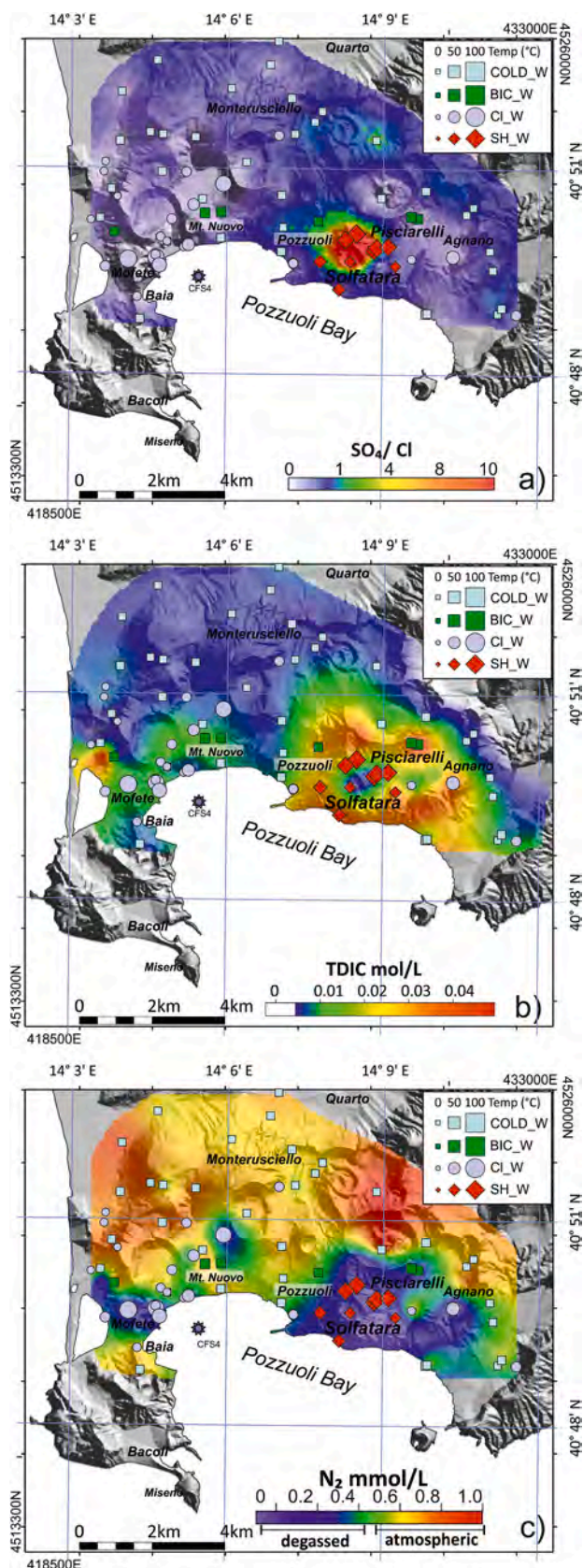


Fig. 9. 3D view of the water table morphology. This exhibits a bell-shaped geometry centered at Solfatara caused by steam condensation of hydrothermal fluids. The vertical section refers to temperatures (°C) resulting from the 3D physical model of the Campi Flegrei geothermal system developed by using the TOUGH2 code simulator (for details see Petrillo et al., 2013).



**Fig. 10.** Maps of (a) SO<sub>4</sub>/Cl ratio in CFC groundwater; (b) total dissolved inorganic carbon (TDIC) concentration in CFC groundwater; and (c) the dissolved nitrogen concentration in CFC groundwater.

meteoric water and (ii) seawater and/or hydrothermally modified seawater, as preliminarily indicated by Fig. 5a and as suggested in earlier studies (Baldi et al., 1975; Valentino et al., 1999; Bolognesi et al., 1986), is inconsistent with the Cl vs.  $\delta^{18}\text{O}$  systematics (Fig. 5b), in which two divergent data trends are observed. In this diagram, the CI\_W are indeed well explained by variable extents of dilution (by meteoric water) of hydrothermally processed seawater (Mofete 1) or pure seawater; however, the SH\_W (and to some minor extent the BIC\_W) align along a nearly horizontal trend that requires an isotopically heavy component that carries essentially zero chlorine. Liquids formed by partial condensation of a Solfatara-Pisciarelli fumarolic steam (Cl ~ 5 ppm; calculated  $\delta^{18}\text{O}$  values of ~0 to +4 ‰) manifest these characteristics. The Fumose submarine vents (CFS samples) plot in an intermediate position between the two trends (Fig. 5b), indicating they experience both (i) mixing with hydrothermal brines/seawater and (ii) steam heating.

## 6.2. Mixing

Volcano-hosted groundwater systems in general (Jasim, 2016), and the CFC thermal groundwater system in particular (Celico et al., 1992; Rolandi and Stanzione, 1993), are complex sequences of superimposed aquifers, hosted in lithologically distinct geological units of different mineralogy/porosity/permeability. Each of these water bodies then evolves its own specific chemical flavor from the peculiar temperature regime, gas-water-rock reaction environment, and meteoric/seawater vs. deep fluid supply. However, geological discontinuities such as faults and fractures locally favor mixing between these distinct water bodies, generating groundwater of hybrid chemistry. Saline hot brines can locally rise to mixed with shallow meteoric-dominated groundwater (Aiuppa et al., 2006), as in the case of CFC (Guglielminetti, 1986; Rosi and Sbrana, 1987; De Vivo et al., 1989; Caprarelli et al., 1997). In the Mofete area (Fig. 1) for example, exploratory geothermal drilling in the 1970s–1980s revealed the existence of three distinct superimposed hot aquifers at depths of 500–900 m (temperatures of 210–250 °C), 1800–2000 m (temperatures of 295–310 °C), and 2500–2700 m (temperatures of 340–360 °C) (Guglielminetti, 1986; see also references in Marini et al., 2022). Upon ascent, these hot reservoir brines can act as sources of dissolved components to shallow thermal groundwater.

Figure 4 explores the mixing relationships between the different water types at CFC using major elements. From this analysis, we propose that a large part of the observed groundwater chemical diversity can be accounted for by mixing – in various proportions – of 6 distinct end-members (compositions listed in Table 1):

- local seawater (SW);
- two low-salinity ( $m_a$ ,  $m_b$  Cl ~ 10 mg/l) endmembers, representing variably mineralized (see their different Na, K and Mg contents) infiltrated meteoric water (see their meteoric O and H isotopic signature; Fig. 5);
- a Cl-poor (~5 mg/l) and SO<sub>4</sub>-rich (~3000 mg/l) component, interpreted as a hydrothermal steam condensate (s.c.) (cfr. 6.1);
- a hot/saline hydrothermal brine component (Fig. 2), here represented by the composition of the Mofete 2 drilling fluids (Cl ~10,000 mg/L) that, from O and H isotopic evidence, can be

**Table 1**

Chemical composition of potential end-members involved in the mixing processes affecting of CF groundwaters. Concentrations are reported in mg/L.

	Na	Cl	Mg	K	SO <sub>4</sub>
Mofete2	5090	10,200	1	1200	30
SW	12,250	22,390	1397	440	2900
$m_a$ COLD_W	100	10	2	5	20
$m_b$ BIC_W	35	10	20	50	20
s.c.	600	10	0.5	1	3000
TC	3000	1500	1	1000	500



interpreted as infiltrated seawater modified by some Solfataralike steam addition (Fig. 5) and water-rock interaction (as indicated by the manifest Mg and  $\text{SO}_4$  depletions relative to seawater; Fig. 4);

- v. a less saline (Fig. 2) hydrothermal component (TC,  $\text{Cl} \sim 1500\text{--}2000$  mg/L), equilibrated at high temperature ( $\sim 350$  °C, Fig. 11), discharged in the Pisciarelli area, mostly represented by the Tennis Hotel sample. From chemical and isotopic point of view, this thermal component can be interpreted as an original mixture of hydrothermal brine (e.g. the liquid encountered in the local CF23 geothermal well; Caliro et al., 2007) with steam condensates.

The relative contributions of the 6 endmembers described above are different in the various water types identified. In particular,  $\text{Cl}_W$  are interpreted to reflect mixing between endmembers local seawater (SW), Mofete brines and meteoric waters ( $m_a$  and  $m_b$ ); while  $\text{SH}_W$  are dominated by end-member *s.c.*, but also receive contributions from the *TC* hydrothermal component and meteoric water ( $m_a$  and  $m_b$ ). These different water types also evolve in distinct thermal regimes, as indicated by comparison with the theoretical compositions of fully equilibrated fluids with reservoir rocks (Giggenbach, 1988, Fig. 11). Plotting our results in Giggenbach's (1988) triangular plot highlights that  $\text{Cl}_W$  reflect equilibrium conditions with the host rocks at  $\sim 140\text{--}160$  °C (well below the Mofete reservoir fluids equilibrated at  $\sim 320$  °C), while  $\text{SH}_W$  fall in the field of immature and/or partially equilibrated waters, with the most Na-rich samples potentially indicating deep equilibrium temperatures in the source reservoir (the *TC* thermal component perhaps?) at 240 to 340 °C (Fig. 11). This behavior could support the existence and mixing of the distinct superimposed hot aquifers found in the Mofete area (Fig. 1) from the exploratory geothermal drillings carried out in the 1970s–1980s (Guglielminetti, 1986; see also references in Marini et al., 2022).

### 6.3. Ingassing and degassing

The infiltrated meteoric waters ( $\text{COLD}_W$ ) that recharge the shallow CFC aquifer system contain a dissolved gas phase of atmospheric origin, as indicated by their high  $\text{N}_2$  and Ar concentrations, and  $\text{N}_2/\text{Ar}$  ratios

close to air or air-saturated groundwater (Fig. 6). However, as these recharge waters enter the core of the hydrothermal system (the inner central portion of the caldera; Fig. 1), they increasingly interact with a deeply sourced,  $\text{CO}_2$ -rich magmatic-hydrothermal vapor phase (Fig. 10b, c). The  $\text{N}_2$  vs. TDIC ( $\text{CO}_2$ ) plot (Fig. 6a) demonstrates this clearly, showing that  $\text{BIC}_W$  exhibit an especially steep negative dependence that implies progressive replacement of atmospheric gases by a  $\text{CO}_2$ -rich magmatic-hydrothermal phase (Fig. 10b). The  $\text{Cl}_W$  and  $\text{SH}_W$  waters exhibit less steep relationships, e.g., more modest  $\text{CO}_2$  increases, indicating dilution by condensed steam in the main hot outflow zone of the Solfataralike “gas plume” (see the  $\text{CO}_2$  relative low in the hot core of the hydrothermal system; compare Fig. 10a and b).

The progressive dissolution of deeply sourced magmatic-hydrothermal volatiles is especially well tracked by He (Fig. 7) and C (Fig. 8) isotopes. The CFC groundwaters are variably enriched in non-atmospheric He, as indicated by their below-air  $\text{Ne}/\text{He}$  (from 0.17 to 13.1) and  $\text{N}_2/\text{He}$  ratios, and  $\text{R}/\text{Ra}$  ratios  $\neq 1$  (Fig. 7). Considering the observed spread of isotope compositions (0.089 to 2.73  $\text{R}/\text{Ra}$ ), we interpret the excess (non-atmospheric) He in our thermal groundwater samples to reflect mixing between (i) a magma-sourced fluid whose He isotope composition is constrained by Solfataralike fumaroles,  $2.85 \pm 0.12$  Ra (Caliro et al., 2014); this range of values agrees with measurements in off-shore gas discharges from the Pozzuoli Bay (0.9–3.1 Ra; Tedesco et al., 1990; Vaselli et al., 2011) and fluid inclusions in olivines and clinopyroxenes from mafic volcanic rocks (2.5–3.0 Ra; Martelli et al., 2004) and (ii) a crustal component with  $\text{R}/\text{Ra} < 0.1$ , perhaps deriving from re-mobilization of radiogenic He ingrowth in the crustal basement. This crustal component is also evident in the TDIC- $^3\text{He}$ - $^4\text{He}$  triangular plot of Fig. 12.

The same plot also shows that the CFC thermal groundwater samples are enriched in  $\text{CO}_2$  relative to He compared to a “magmatic” end-member exemplified by the Solfataralike fumarolic gas. Since  $\text{CO}_2$  is more soluble in water than He (Ballentine et al., 2002), selective/preferential He loss upon water decompression and degassing during groundwater ascent (to surface discharge at atmospheric pressure) can explain the  $\text{CO}_2/\text{He}$  mismatch between groundwater and fumaroles. It is also possible, however, that some of the excess  $\text{CO}_2$  derives from remobilization of hydrothermal calcite, as recently proposed (Chiodini et al., 2015; Buono et al., 2023).

The overall message recorded by dissolved gases is hence that of a

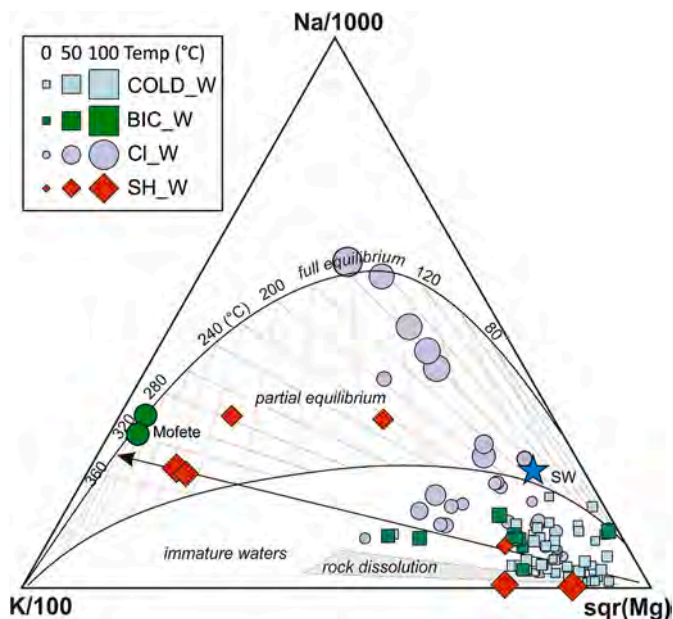


Fig. 11. Ternary Na-K-Mg geothermometric diagram (modified from Giggenbach, 1988). Temperatures as high as 340 °C are estimated for samples discharged at Pisciarelli.

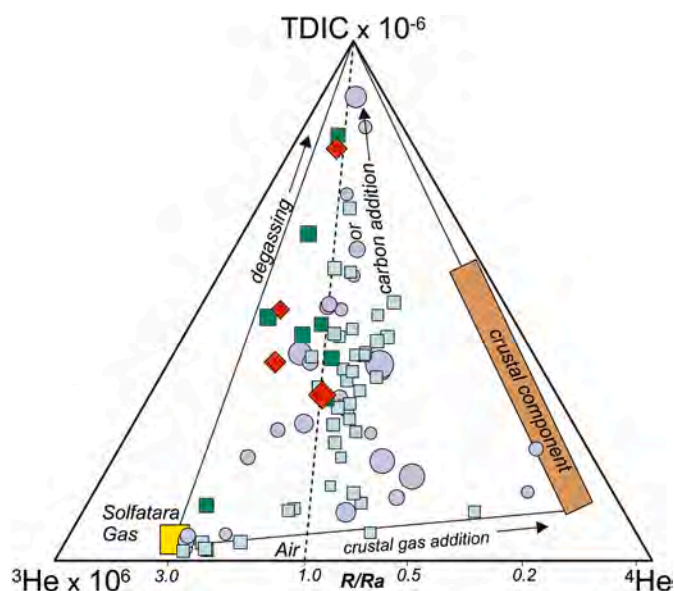


Fig. 12.  $^3\text{He}$ - $^4\text{He}$ -TDIC triangular plot showing the compositional diversity of dissolved gases in the CFC groundwater. The compositions of possible gas sources involved in mixing processes are also indicated.

multi-step process, starting with (i) the initial infiltration of air-saturated groundwater, followed by (ii) pressurization by dissolution (ingassing) of a CO<sub>2</sub>-He-rich magmatic-hydrothermal vapor during downward water inflow in the caldera central segment, eventually with some addition of crustal gases (for both CO<sub>2</sub> and He), and finally (iii) degassing of more water-insoluble species (He, N<sub>2</sub>, Ar, CH<sub>4</sub>) during groundwater upflow and decompression to 1 bar.

We model this sequence of processes by applying a gas-water-rock reaction-path model that numerically simulates the interaction among water, gas and rock within the shallow volcanic aquifers. The model simulates the evolution of the chemical and carbon isotopic composition of groundwater affected by the input of a hydrothermal Solfatara-like CO<sub>2</sub>-rich gas phase. The simulation has been done by use of the PHREEQC code (Parkhurst and Appelo, 1999), associated with a VBA (Visual Basic for Application) script to write the input file, run the executable code, read and elaborate the output files, and compute the carbon isotopic composition of each carbon species (in solution and degassed) at each step of the model. The PHREEQC database has been integrated with thermodynamic data of the investigated gas species (N<sub>2</sub>, O<sub>2</sub>, Ar, Ne, He) taken from Wilhelm et al. (1977) and considered as non-reactive species in the models. Rigorous simulation of water-rock interaction would require considering dissolution of primary minerals and formation of alteration minerals. However, for simplicity, we approach the simulation not relying on a purely thermodynamic approach, but rather based on empirical functions established from the chemical composition of the investigated groundwater (Fig. 13). In particular, to quantify the interaction between water, rocks and hydrothermal gas during the reaction pathway modelling, we utilize the relationship between carbonate bound cations (CBC) and the corresponding TDIC value (Fig. 13). CBC quantifies the extent of dissolution of primary volcanic minerals, and is computed by subtracting the sum of chloride, nitrate and sulphate equivalents from the sum of Ca, Mg, Na and K. In other words, CBC corresponds to alkalinity in charge-balanced analysis. TDIC is computed at discharged condition for the samples undersaturated with respect to calcite and, for the samples oversaturated with respect to calcite, TDIC is computed by bringing the solutions back to equilibrium conditions with respect to calcite by adding CO<sub>2</sub> (see Caliro et al., 2005).

The model simulates the composition of major ions, dissolved gases, and their isotopic compositions at depth (RC, reservoirs conditions) and

**Table 2**

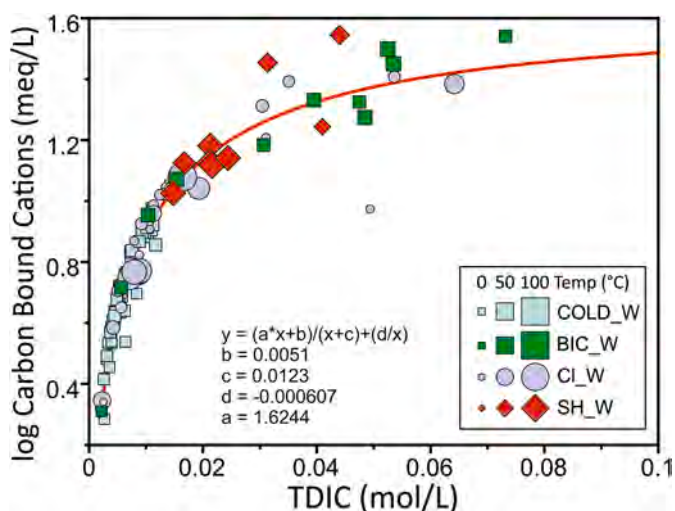
The average composition of Solfatara BG fumarole in 2013. Concentrations are in μmol/mol. Carbon isotopic composition is expressed in delta notation per mill vs. V-PDB;

CO <sub>2</sub> (g)	2.57E+05
Ar(g)	6.36E-01
N <sub>2</sub> (g)	4.99E+02
He(g)	2.47E+00
Ne(g)	8.22E-03
δ <sup>13</sup> C	-1.3‰

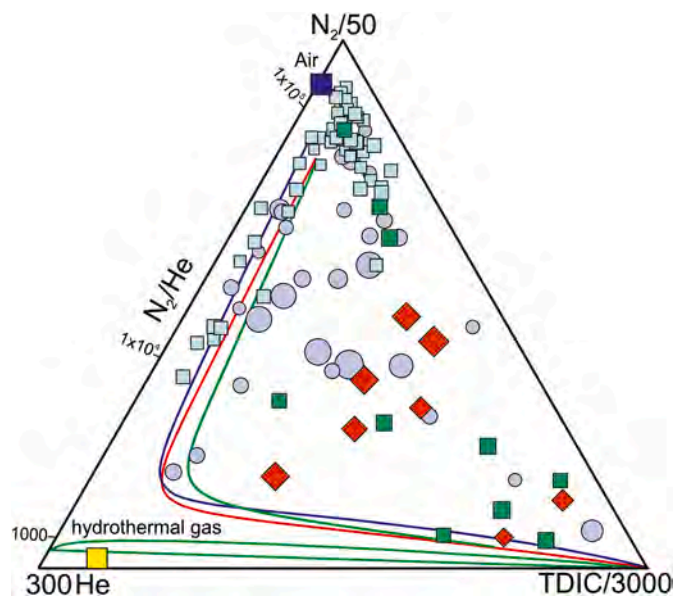
at the surface (ES, emergence conditions). Deep conditions are simulated assuming that no chemical and isotopic fractionation occurs during addition of gases to the solution (for more details see Wigley et al., 1978, 1979). Degassing does not take place at this stage because of the relatively high hydrostatic pressures. While approaching emergence/spring conditions, the solution is allowed to degas in chemical and isotopic equilibrium at decreasing pressures in a multistep process from condition reached at depth to a gas pressure of 1 bar at the surface. For the samples that are supersaturated at emergence conditions, the minimum pressure at reservoir conditions can be estimated by bringing the sample back into equilibrium with respect to the calcite.

The CFC solution carbonate system shows that the samples exhibiting low TDIC concentrations have negative δ<sup>13</sup>C values (δ<sup>13</sup>C < ~ -10 ‰), while samples with higher TDIC have the most positive δ<sup>13</sup>C values (Fig. 8). This behavior implies the presence of different carbon sources. Carbon-13-depleted composition suggests a biologic origin, while more positive δ<sup>13</sup>C values (<sup>13</sup>C enriched) might indicate a deep magmatic/hydrothermal source, similar to the fumarolic fluids emitted at Solfatara (δ<sup>13</sup>C -1.3 ‰ Caliro et al., 2007).

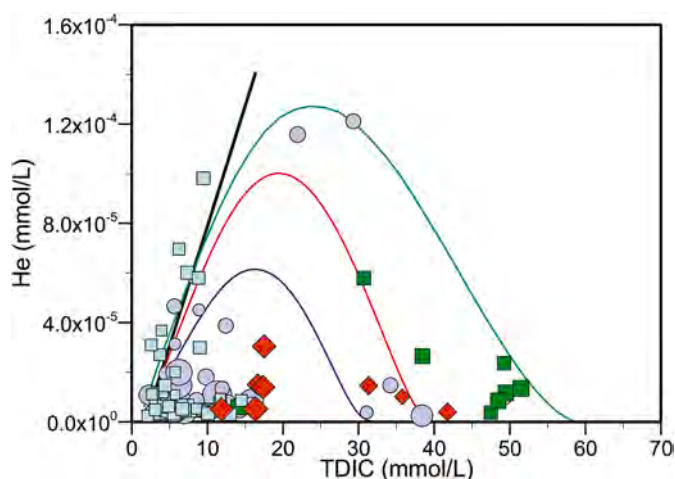
We start the models by equilibrating a meteoric water with a TDIC of ~1 mmol/L and δ<sup>13</sup>C of -8 ‰ at 1 bar and 20 °C with atmospheric components (N<sub>2</sub>, O<sub>2</sub>, Ar, He). CO<sub>2</sub> with biologic isotopic composition from δ<sup>13</sup>C -25 ‰ to -15 ‰ is systematically added to this solution (Fig. 8). Most of the bicarbonate cold waters (Fig. 8) are in agreement



**Fig. 13.** Log concentrations of Carbon Bound Cations ( $\sum(\text{Ca, Mg, Na, K}) - \sum(\text{Cl, NO}_3, \text{SO}_4)$ ) in meq/L vs. TDIC. The relation (red line) was used in the reaction-path modelling to compute the amount of carbonate bound cations dissolved by the addition of the deep gas phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 14.** Dissolved gas species N<sub>2</sub>, He and TDIC in CFC groundwater showing compositional evolution lines resulting from the models. The models start from the N<sub>2</sub>-rich air/asw composition. Hydrothermal gas input moves compositions towards a He-rich composition until degassing becomes predominant, resulting in loss of He and enrichment of carbon species. Light green lines indicate the composition of the degassed gas phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 15.** He vs. TDIC concentrations in the CFc groundwater. Conditions modeled in the reservoir (black line) and the lines resulting after degassing to atmospheric pressure are also reported. The addition of gases to the solution, and the consequent increase of solution temperature, increase the gas-pressure, inducing degassing and in particular He loss, as shown by the BIC\_W and SH\_W groundwaters, respectively.

with these models, indicating input of biogenic carbon, while the other water types require a distinct carbon source. Using as starting solutions the compositions at 2 and 3 mmol/L of TDIC obtained in the previous model (−25 %), three simulations were done at different temperatures (25–60–80 °C; Fig. 8) adding to the solutions a hydrothermal Solfataralike gas phase with composition reported in Table 2. 0.1 mol of this gas phase are added to the solution in 100 steps, adding CBC to the solution following the relation of Fig. 13. At each step, after dissolution of the gas phase, the solution is allowed to degas to atmospheric pressure. The model lines reported in Figs. 8, 14 and 15 refer to the solutions after degassing at discharge conditions (PHREEQC files for the 60 °C model are in the Supplementary Material S2 and S3).

Most of the water samples are in good agreement with the proposed models, showing that a combination of (i) input of a Solfataralike hydrothermal gas phase and (ii) degassing from reservoir conditions to the shallow conditions can account for the dissolved gas and dissolved

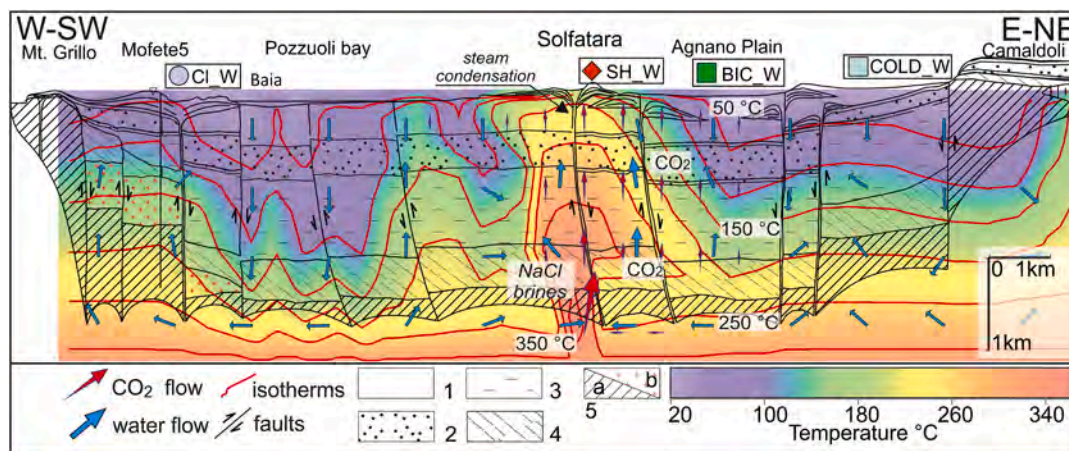
carbon isotopic compositions. Data variability of samples plotting out of the modelling lines can be explained by the mixing process, as discussed in the previous sections.

## 7. Conclusions and implications for volcano monitoring

We have shown here that the large diversity in groundwater composition at CFc reflects the combined action of a variety of processes, including (i) infiltration of shallow meteoric/marine waters in the aquifer(s), (ii) their chemical processing and maturation, initiated by the dissolution of deeply sourced magmatic volatiles, and modulated by the mixing with hydrothermal brines ascending from deeper hydrothermal reservoirs, and (iii) further chemical evolution during upward groundwater flow (to the emission/sampling point), primarily driven by degassing of poorly soluble gases ( $N_2$ , Ar, He,  $CH_4$ ) and condensation of hot hydrothermal steam (primarily in the Solfataralike sector). These processes act in concert, but their relative roles vary in space determining the chemical heterogeneity of the aquifer system, as summarized in the cross-section of Fig. 16. This Figure also illustrates the estimated temperature and fluids circulation patterns resulting from the 3D physical modelling of the CFc hydrothermal system (Petrillo et al., 2013). This scheme also emphasizes the role of volcano-tectonic structures (taken from a WSW-ENE section of Orsi et al., 1996) in controlling the migration of fluids ( $CO_2$  gas and aqueous solutions), as inferred from the physical model of CFc hydrothermal system (Petrillo et al., 2013).

The processes depicted in Fig. 16 may also vary in time if the ongoing unrest escalates further. This aspect is especially valuable in terms of volcano monitoring because, as seen elsewhere (see review in Jasin et al., 2018), any change in groundwater composition would ultimately respond to changes in hydrothermal regime, and hence in caldera activity state.

The Solfataralike district has recently experienced remarkable changes in hydrothermal activity, with notable variations in fumarole composition (Chiodini et al., 2016, 2021, 2022; Cairo et al., 2025) and increases in the  $CO_2$  output from soil diffuse degassing (Cardellini et al., 2017) and fumaroles (Aiuppa et al., 2013; Tamburello et al., 2019). Taken together, these observations imply an escalating transport of magma-sourced volatiles to the Solfataralike hydrothermal system (Chiodini et al., 2022), causing pressure build-up at depth (Chiodini et al., 2021) and hence rock failure (the Solfataralike zone and its surroundings are the areas where the majority of the CFc seismicity is



**Fig. 16.** Conceptual model for the diversity of CF groundwaters in the context of the results of the 3D physical model of the Campi Flegrei geothermal system (Petrillo et al., 2013). The geological section of the CF caldera, shown as background, is from Orsi et al. (1996). The main processes concurring to the definition of chemical and isotopic composition of groundwater and thermal water are also indicated. The predominant effect on the fluids circulation is represented by a central plume below the Solfataralike crater that activate convective cells, producing variable patterns of gas, liquid and temperature inside the hydrothermal system. Geological section (modified after Orsi et al., 1996): (1) Volcanics and marine sediments younger than 15 ka; (2) Neapolitan Yellow Tuff (NYT); (3) Volcanics and marine sediments emplaced between 39 and 15 ka; (4) Campanian Ignimbrite (CI); (5) Rocks older than 39 ka, a) pyroclastics, b) lavas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

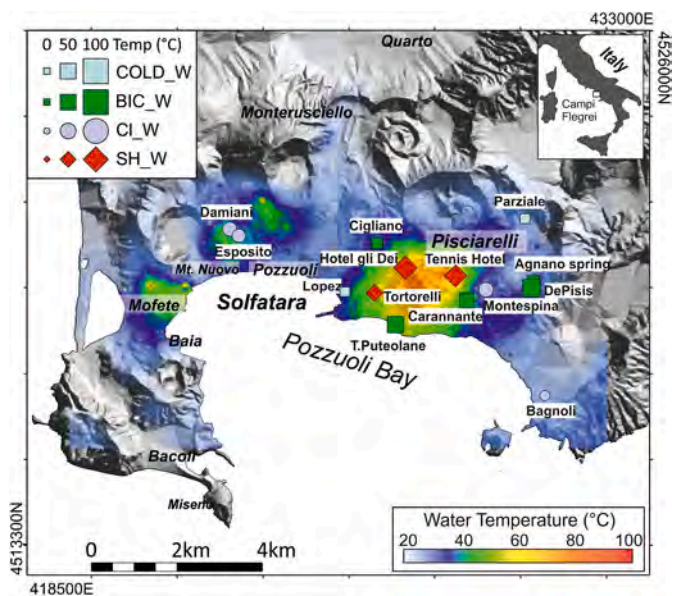


Fig. 17. Multi-parameter groundwater monitoring network (temperature, salinity and piezometric level) consisting of 14 stations covering a wide area surrounding Solfatara, active since 2018. Symbols as in Fig. 2.

clustered; Scarpa et al., 2022; Giacomuzzi et al., 2024).

In response to the increase in volcanic activity and in order to improve the monitoring network system within the agreement for the Seismic and Volcanic Surveillance between the Italian Department of Civil Protection and the INGV (National Institute of Geophysics and Volcanology), since 2018 a permanent network of stations for continuous multi-parametric monitoring of the CF groundwater has been developed and implemented at CFC (Fig. 17). The installed CTD systems have shown excellent sensitivity and stability over time, allowing to identify seasonal variations, linked to meteorological events. Moreover, data recorded by this network allowed to recognize rapid changes in water temperature, water level and salinity in response to phases of especially intense seismicity activity and accelerating ground deformation, which are the subject of ongoing investigation (and will be presented elsewhere).

We have shown here that groundwater chemistry in the Solfatara-Pisciarelli district is primarily controlled by near-surface condensation of the hydrothermal steam plume feeding the Solfatara fumaroles. We argue then that continuous measurement of groundwater temperature, piezometric level and conductivity in this area may reveal critical to identifying any further escalation in hydrothermal steam transport, would the degassing unrest intensifies further. In more marginal areas relative to center of deformation (Pozzuoli city) and degassing (Solfatara-Pisciarelli), such as in the Agnano plain and in the Baia-Monte Nuovo sectors (Fig. 1), the chemistry of thermal groundwater primarily reflects the addition of deeply sourced  $\text{CO}_2$  (BIC\_W) and mixing with deeply rising (Mofete reservoir-like) hydrothermal brines (CI\_W). In these sectors, permanent groundwater monitoring (Fig. 17) may help identifying any stress change and/or change in fluid circulation pathways, and especially if the mixing proportions between different water types, or the supply of deeply sources gases/brines, vary in time in response to changes in the hydrothermal-magmatic system underneath. Visible variations in well water outflow and temperature have been documented in historical records prior to the last CFC eruption in 1538 AD (Guidoboni and Ciuccarelli, 2011), which adds confidence on the ability of a modern instrumental network (as the one implemented at CFC; Fig. 17) to detect any further change in hydrothermal regime.

## CRediT authorship contribution statement

**Stefano Caliro:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization, Supervision. **Rosario Avino:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Francesco Capecciacci:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Antonio Carandente:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Giovanni Chiodini:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Emilio Cuoco:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Carmine Minopoli:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Francesco Rufino:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Alessandro Santi:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Andrea L. Rizzo:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Alessandro Aiuppa:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization, Supervision. **Vincenzo Allocca:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Pantaleone De Vita:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Mauro A. Di Vito:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Stefano Caliro reports financial support was provided by Dipartimento della Protezione Civile, Presidenza del Consiglio dei Ministri. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jvolgeores.2025.108280>.

## Data availability

Data used in this work are uploaded as S1 table; input and output file of the proposed model are reported as S2 and S3 supplementary material, respectively.

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