The Hydrothermal System of the Campi Flegrei Caldera, Italy

Giovanni Chiodini, Stefano Caliro,
Rosario Avino, Emanuela Bagnato,
Francesco Capecchiacci, Antonio Carandente,
Carlo Cardellini, Carmine Minopoli,
Giancarlo Tamburello, Simona Tripaldi,
and Alessandro Aiuppa

Abstract

In this chapter, we review the state-of-the-art of the Campi Flegrei caldera (Naples) hydrothermal system, and its behaviour during the last decades. The Campi Flegrei caldera has been undergoing unrest since 1950, as evidenced by recurrent bradyseismic episodes accompanied by manifest changes in the degassing budget, degassing patterns and in the composition of the fumarolic fluids. In-depth analysis of geochemical and geophysical datasets acquired over decades has allowed identification of the mechanisms driving volcanic unrest at the Campi Flegrei caldera. We propose a conceptual model of the hydrothermal system feeding Solfatara fumaroles, where geochemical information is integrated with Audio Magneto Telluric measurements, which yields a realistic picture of the geometry of the system up to a depth of 2.5 km. The model identifies a ∼2 km elongated vertical high resistivity structure in axis with the Solfatara fumaroles, which represents a relatively high permeability zone allowing hot fluid ascent from depth to the shallower portions of the hydrothermal system. Pulsed injections of hot magmatic fluids (CO_2-rich and CH_4-poor oxidised fluids) at the bottom of the hydrothermal system is thought to be one of the key processes that has controlled the evolution of the system during the last 40 years. The episodes of injection of magmatic fluids changed in frequency and intensity during time, ultimately causing an overall heating and pressurisation of the system since the early 2000s, as reflected by escalating degassing flux, increase in areal extension of the degassing areas, and in the composition of the fumaroles. In particular, the CO_2/CH_4 and He/CH_4 ratios of fumarolic fluids exhibited recurrent peaks, marking the episodes of injection of magmatic fluids. Moreover, the quasi-monotonic increasing trend of the fumarolic CO_2/H_2O ratio, from 0.15 to 0.18 in 2000 to ∼0.4 in 2018–2019, has been interpreted as due to the combined action of partial steam condensation, and CO_2

G. Chiodini (✉) · C. Cardellini · G. Tamburello
Istituto Nazionale di Geofisica e Vulcanologia,
Sezione di Bologna, Bologna, Italy
e-mail: giovanni.chiodini@ingv.it

S. Caliro · R. Avino · E. Bagnato · F. Capecchiacci ·
A. Carandente · C. Minopoli
Istituto Nazionale di Geofisica e Vulcanologia,
Sezione Osservatorio Vesuviano, Napoli, Italy

C. Cardellini
Dipartimento di Fisica e Geologia, Università degli
Studi di Perugia, Perugia, Italy

S. Tripaldi
Dipartimento di Scienze della Terra e Geoambientali,
Università degli Studi di Bari Aldo Moro, Bari, Italy

A. Aiuppa
Dipartimento di Scienze della Terra e del Mare,
Università degli Studi di Palermo, Palermo, Italy

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addition from a magmatic source and possibly from de-carbonation of hydrothermal calcite favoured by the heating of the hydrothermal reservoir. These changes strongly suggest that the ongoing (since 2000) unrest is triggered by a degassing magma source, but also that the system's response is modulated by dynamics and structures of the overlying hydrothermal envelope. This evolution clearly requires careful scientific scrutiny and intensified monitoring in the years to come.

1 Introduction

The bradyseismic crises that started in the mid-1900s (Del Gaudio et al. 2010), and that in 1983–1984 caused the evacuation of the Pozzuoli town (Fig. 1) (Barberi et al. 1984), have prompted an increasing number of studies aiming at shading light onto the structure, chemical properties and temporal evolution of the hydrothermal system(s) hosted within the Campi Flegrei caldera (CFc). For a synthesis of the volcanic and deformation history and of the geophysical structure of the caldera see Chaps. Volcanic and Deformation History of the Campi Flegrei Volcanic Field, Italy; Seismic and Gravity Structure of the Campi Flegrei Caldera, Italy, respectively. Magmatism and volcanism of the structure were fed by a complex system whose architecture, behaviour and evolution are summarised in Chaps. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data; Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data; Tephrochronology and Geochemistry of Tephra from the Campi Flegrei Volcanic Field, Italy; Rheological Properties of the Magmas Feeding the Campi Flegrei Caldera (Italy) and Their Influence on Mixing Processes; Magma Chamber Dynamics at the Campi Flegrei Caldera, Italy. For reviews of the results of the monitoring network and time variation of the physical parameters of the short-term deformation see Chaps. The Permanent Monitoring System of the Campi Flegrei Caldera, Italy; Historic Unrest of the Campi Flegrei Caldera, Italy; Source Modelling from Ground Deformation and Gravity Changes at the Campi Flegrei Caldera, Italy.

Knowledge of hydrothermal fluid circulation in the subsurface of Campi Flegrei was initially obtained from geothermal wells drilled in the 1950's (Penta 1954) and subsequently in the 1970's–early 1980's (Guglielminetti 1986). These drilling projects offered insights into the deep structure of CFc (Rosi and Sbrana 1987; De Vivo et al. 1989), and have revealed the existence of a saline multiple-reservoir field (sub-surface temperatures of 250–390 °C) composed of at least two distinct reservoirs fed by seawater (<2,000 m) and meteoric-magmatic fluids (>2,000 m) (Caprarelli et al. 1997). These deep reservoirs would supply magmatic volatiles and heat to the shallow groundwater system, whose surface manifestations (thermal wells and subaerial/submarine thermal springs; Martini et al. 1991; Celico et al. 1992; Valentino et al. 1999; Valentino and Stanzione 2003, 2004; Aiuppa et al. 2006; Di Napoli et al. 2016) generate a manifest thermal anomaly in the caldera's centre, in the surroundings of the Solfatara area (Fig. 1). The post-1980s clustering of degassing activity (Chiodini et al. 2001, 2005, 2010; Aiuppa et al. 2013), seismicity (Chiodini et al. 2017a; Giudicepietro et al. 2017; Di Luccio et al. 2015) and deformation (Del Gaudio et al. 2010) within (or nearby) the same Solfatara area, has motivated extensive research on the chemistry, isotope composition and flux of fluids discharged by its fumarolic field (Cioni et al. 1984; Chiodini et al. 2003, 2010, 2015a, b, 2016; Caliro et al. 2007, 2014; Cardellini et al. 2017). In this review, we concentrate on hydrothermal fluid circulation beneath Solfatara.

Solfatara is a tuff cone dated at 4,181–4,386 cal. years BP (Smith et al. 2011 and references therein; Chap. Volcanic and Deformation History of the Campi Flegrei Volcanic Field, Italy), whose volcanic products are strongly hydrothermally altered by pervasive circulation of hydrothermal fluid and intense CO_2 diffuse degassing from hot soils (Rosi and Sbrana 1987;

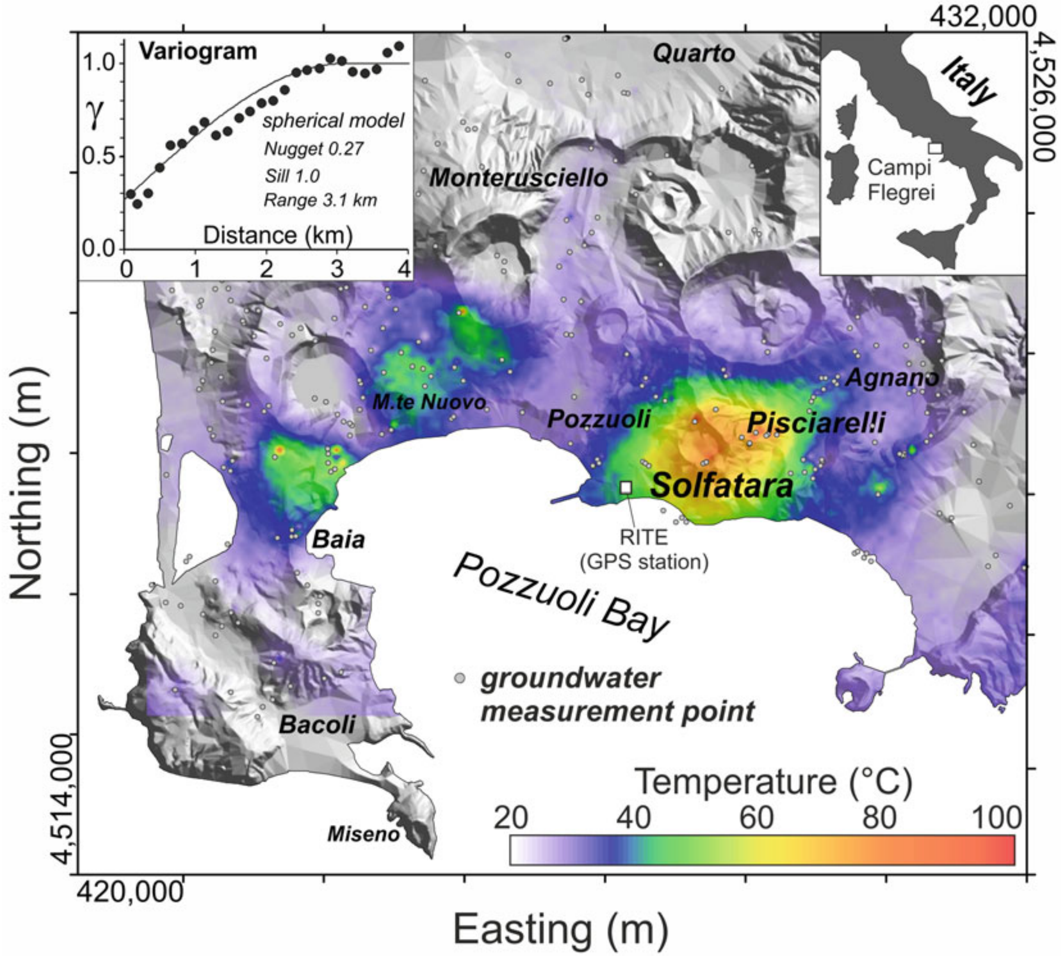


Fig. 1 Temperature distribution of the Campi Flegrei groundwaters. The map was produced using the Sequential Gaussian Simulation algorithm (Deutsch and Journel 1998) based on a dataset of 290 water temperatures, most of them refers to shallow wells with variable depths, generally lower than 100 m. Data from Petrillo et al. (2013), and data collected by Istituto Nazionale di Geofisica e Vulcanologia—Osservatorio Vesuviano in the period from 2013 to 2018. Coordinates expressed in metres refer to the UTM WGS84

Chiodini et al. 2001; Fig. 1). The crater and its surroundings host one of the better studied fumarolic fields of the world, with a fairly continuous and systematic record of geochemical data (acquired together with geophysical signals) dating back to the large 1983–1984 bradyseismic crises (e.g., Carapezza et al. 1984; Cioni et al. 1984; Tedesco et al. 1990; Allard et al. 1991; Chiodini and Marini 1998; Panichi and Volpi 1999; Tedesco and Scarsi 1999). In detail, an exceptionally long (~35 years) record of the chemical and isotopic compositions of fumaroles is available for the Solfatara (Chiodini et al. 2016; Istituto Nazionale di Geofisica e Vulcanologia—Osservatorio Vesuviano unpublished data), together with ~20 years of diffuse soil emission measurements of volcanic-hydrothermal CO_2 (Cardellini et al. 2017). In-depth analysis of this huge and unique dataset, acquired over decades of recurrent seismicity and ground deformation episodes, has been central to identifying the causal mechanisms driving volcanic unrest at CFc. The key conclusion that has arisen from these investigations is that observed indicators of volcanic unrest (escalating deformation, seismicity and degassing) are all caused by repeated pulses of hot magmatic fluid injection into the hydrothermal system feeding the Solfatara (e.g., Chiodini et al. 2003, 2012, 2016).

The aim of this chapter is to review our current understanding of the Solfatara hydrothermal system, putting the accent on both subjects where there is an agreement within the scientific community, and arguments that have remained intensely debated in the scientific community.

2 Mass and Energy Release at Solfatara

The Solfatara crater and its surroundings are home to numerous thermal manifestations, including fumarolic vents, boiling pools and hot soils diffusively degassing CO_2. In particular, the Solfatara hydrothermal system sustains one of the most actively degassing and well-characterised diffuse degassing structures (Chiodini et al. 2001) worldwide. Here, we refer to the work of Cardellini et al. (2017) that reports and discusses in detail the results of 30 surveys of soil diffuse CO_2 flux carried out at Solfatara from 1998 to 2016 using the accumulation chamber method (Chiodini et al. 1998). Each survey consisted of several hundred measurements (typically 400–500) and covered a ~1.2 × 1.2 km^2 area. Cardellini et al. (2017), using the measurements of all the different campaigns (13,158 points), produced a very detailed image of the Solfatara diffuse degassing structure (DDS; Fig. 2). With the term Solfatara DDS we refer to the sector that, during the observation period, released volcanic-hydrothermal CO_2, either continuously or sporadically. The Solfatara DDS (yellow–red colours in Fig. 2) includes both the crater and sectors external to the cone, such as the Pisciarelli, Monte Olibano and via Antiniana areas (Fig. 2). It is worth noting that the geometry of the DDS correlates well with the main volcanic and extensional tectonic structures (northwest-southeast and northeast-southwest lineaments) channelling gas transfer from depth towards the surface.

The areal extent of the Solfatara DDS, and the total amount of CO_2 released by diffuse soil degassing, both varied considerably over time. The DDS surface increased from 0.45 km^2 in 1998 to more than 1 km^2 in many post-2012 surveys, and the total CO_2 flux consistently increased from ~750 td^{-1} to ~2,800 td^{-1} (Cardellini et al. 2017). The total CO_2 output includes both the deeply derived gas and that produced by biological activity in the soil. However, biogenic CO_2 output has been shown to account for only a few percent of the total release, using carbon isotopic composition of the CO_2 efflux (Chiodini et al. 2008; Cardellini et al. 2017). The diffuse CO_2 output at Solfatara is remarkably high, considering that its mean value (1,309 td^{-1}) is similar to the CO_2 flux to the atmosphere of a “medium-large” volcanic plume, while the maximum measured value (2,800 td^{-1}) would constitute the eighth highest CO_2 flux among volcanic plumes worldwide (see Table 2 in Burton et al. 2013).

The thermal energy release associated with the CO_2 emissions was estimated, in 1998, at ~100 MW (Chiodini et al. 2001). Assuming this value as representative of the last 40 years, the energy associated with diffuse degassing would represent the main component of the CFc energy budget, as it is higher than i) the heat released by conduction over the entire caldera, ii) the energy associated to ground deformations, and iii) the elastic energy released by earthquakes (see discussion in Chiodini et al. 2001, 2017a).

3 Origin of the Solfatara Fluids Based on Fumarole Chemical and Isotopic Composition

The majority of the available information on the CF hydrothermal system stems from detailed analysis of the chemical and isotopic composition of the Solfatara fumaroles. Three of the numerous fumarolic vents located in the Solfatara DDS have temperatures above the water boiling point (Bocca Grande—BG, 150–165 °C; Bocca Nuova—BN, 140–145 °C; Pisciarelli—Pi, 95–120 °C; Fig. 2), and have been routinely

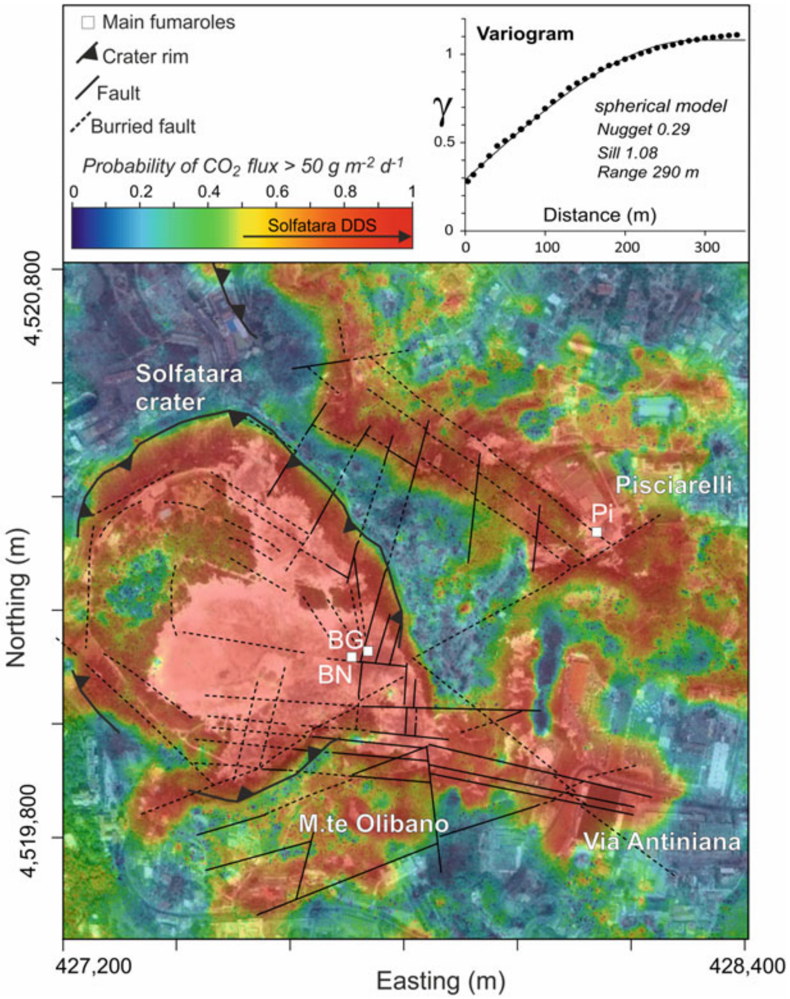


Fig. 2 Map of the Solfatara diffuse degassing structure (DDS). The map was realised by sequential Gaussian simulations (Deutsch and Journel 1998; Cardellini et al. 2003) based on the entire dataset of CO_2 fluxes from 1998 to 2016. The different colours represent the probability that the simulated CO_2 flux is greater than the biogenic threshold of 50 $gm^{-2}d^{-1}$ (Chiodini et al. 2008). Yellow to red colours indicate at each location probabilities higher than 0.5 of CO_2 flux > threshold, highlighting the areas where degassing of deeply derived CO_2 occurs (the Solfatara DDS). The Solfatara DDS well matches the volcano-tectonic lineaments of the area (Isaia et al. 2015). The locations of the main fumaroles, Bocca Nuova (BN), Bocca Grande (BG) and Pisciarelli (Pi) are reported. Coordinates are reported as meters projection UTM European Datum 50. The base map is from http://mapmaker.nationalgeographic.org/ (see Cardellini et al. 2017 for further details)

sampled and analysed in the frame of CFc volcanic surveillance. The BG highest temperature fumarole (Fig. 2), is thought to be the most representative of the deep fluids because it is less affected by shallow secondary processes (Gresse et al. 2018). Its composition is dominated by water vapour (X_{H_2O} from 0.73 to 0.87) and subordinately CO_2 (X_{CO_2} from 0.13 to 0.26). Other analysed species (including H_2S, N_2, H_2, CH_4, He, Ar and CO) exhibit concentrations ranging from less than 1 ppm (CO) to 1,000–2,000 ppm (H_2S).

Magmatic gas supply to the Solfatara hydrothermal system is supported by its fumaroles' stable water isotopes. Steam deuterium and ^{18}O compositions, once corrected for oxygen

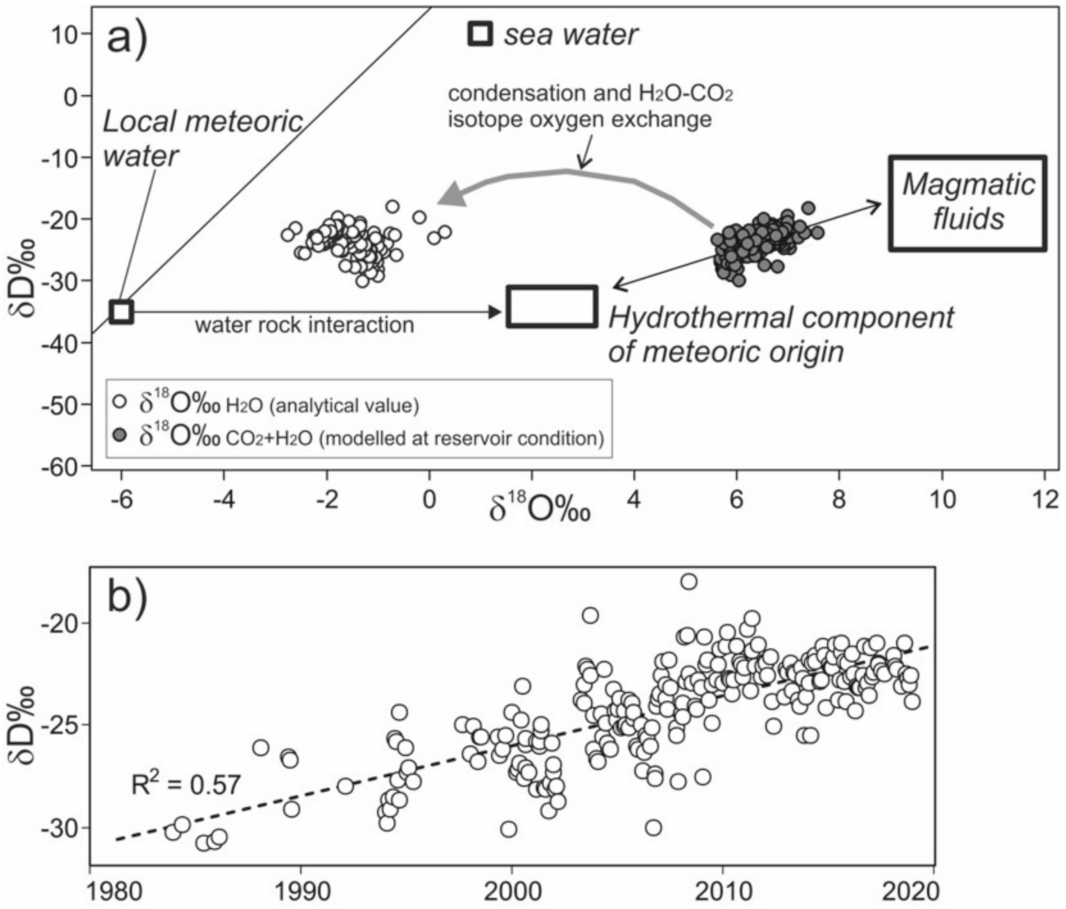


Fig. 3 **a** δD vs $\delta^{18}O$ diagram (modified after Chiodini et al. 2016). Starting from the analytical values (post-2000 samples of BG fumaroles), the equilibrium $\delta^{18}O - \delta D$ composition of hydrothermal vapour (H_2O + CO_2) was calculated considering: reservoir temperatures (Tr), reservoir CO_2 molar fractions (X_{CO_2}), and the fractions of steam (f) that condenses passing from reservoir to discharge. According to Chiodini et al. (2015a), Tr, X_{CO_2} and f were estimated applying gas equilibria in the H_2O-H_2-CO_2-CO gas system. Computations involved solving a set of isotope mass balance and fractionation equations. Fractionation during water condensation and H_2O-CO_2 isotope oxygen exchange (Chiodini et al. 2000) were taken into account. The re-computed $\delta^{18}O$ values refer to the whole CO_2 + H_2O system. The 'Magmatic fluids' box refer to the Giggenbach (1992) andesitic water (δD from −10‰ to −20‰ and $\delta^{18}O$ from + 9‰ to +12‰) **b** Chronogram of the deuterium composition of BG condensates (data from Chiodini et al. 2016)

isotopic exchange between water vapor and CO_2 (Chiodini et al. 2000) and for partial H_2O removal by condensation, clearly depict a mixture between a classical magmatic component and hydrothermal fluids of meteoric origin (Fig. 3a).

The proportion of magmatic fluids in the mixture feeding the Solfatara fumaroles has increased in time, as suggested by δD values increasing from -30% in the early 1980's (close to the local meteoric waters values of δD ∼ −35‰; Panichi and Volpi 1999) to more magmatic values (−25‰ to −20‰) in the post-2010 samples. This temporally increasing fraction of magmatic gas has paralleled with the escalating hydrothermal fluid output (see above) and the generally heating/pressurisation of the system, as derived from interpretation of gas equilibria (see Sect. 6).

A magmatic gas feeding into the hydrothermal system is also consistent with the isotopic signatures of fumarolic CO_2, He and N_2. The carbon isotopic composition of CO_2 ($\delta^{13}C$ = −1.3 ‰ ± 0.4‰; Caliro et al. 2014) supports a mantle source contaminated by crustal fluids delivered by a carbonate-rich subducted slab. The Solfatara CO_2 has, in fact, carbon isotope signature heavier than primary mantle carbon ($\delta^{13}C$ = -6 ‰ ± 2 ‰; Deines and Gold 1973), and lighter than those derived by crustal de-carbonation of marine limestone. It cannot be ruled out, however, that part of the emitted C is derived by de-carbonation of hydrothermal calcite, which is well present in the subsurface at CF, and which may have acted as a source and sink over the geological history of the caldera (Chiodini et al. 2015b). The $^3He/^4He$ ratio measured in the fumaroles (2.85 ± 0.12 R/Ra; Caliro et al. 2014) indicates a significant contribution of primordial (mantle-derived) ^3He, variably contaminated by crustal ^4He (Allard et al. 1997; Tedesco 1997). According to Martelli et al. (2004) these relatively low $^3He/^4He$ ratios, which are close to those measured in the olivine and pyroxenes of the volcanic products, do not result from shallow magma contamination, but rather reflect the composition of the mantle beneath the region. This is thought to have been metasomatised by the addition of crustal fluids from the subducted plate (Martelli et al. 2004; Peccerillo and Frezzotti 2015). The $\delta^{15}N$ of N_2, routinely analysed since 2007, points to a stable positive value of 6.3‰ ± 0.3‰ (Caliro et al. 2014), a value that is compatible with the nitrogen isotopic signature of the fluids emitted by volcanoes located in subduction zones (e.g., Guatemala volcanic arc; Fischer et al. 2002). Finally, the fumarolic He-Ar-N_2 relative compositions are similar to those discharged by the other volcanoes in the region (Vesuvio, Ischia; see Fig. 8 in Caliro et al. 2007) and point to magmatic fluid delivery from the metasomatised local mantle.

To summarise, consensus exists for a deep magmatic fluid feeding the hydrothermal system, followed by mixing with a shallower meteoric hydrothermal component. In this context, extensive scrubbing of hot magmatic gases within the hydrothermal environment would cause removal of original acidic species such as SO_2 (Cioni et al. 1984; Chiodini et al. 2001; Caliro et al. 2007). Sulphur gases are in fact present in detectable amount only as H_2S whose concentrations are controlled by reaction in the shallower part of the hydrothermal system (Chiodini et al. 2012). This hydrothermal control on sulphur species explains the very high C/S of the Solfatara fumaroles (100–200) with respect to ratios of 2 to 4 typical of magmatic fluids (Aiuppa et al. 2017).

4 Temperature–Pressure Estimation Based on Gas Equilibria

Since the 1980s, one of the major objectives of volcanic gas research at CF has been to extract information on temperature and pressure of the hydrothermal system from fumarolic composition (e.g., Cioni et al. 1984; Chiodini et al. 1992, 1996; Chiodini and Marini 1998). Early efforts were based upon resolving gas equilibria within the H_2O-H_2-CO_2-CO-CH_4 gas system, which has exhibited large variations during 1983–2016. A common conclusion reached by these initial studies, which is still valid today, is that the Solfatara fumaroles discharge fluids derived from (and equilibrating within) a vapour-dominated (liquid-free) zone. This distinctive vapour-dominated source area is in contrast with what found at the majority of the world’s hydrothermal systems, whose surface gas manifestations are fed instead by boiling hot liquids (Chiodini and Marini 1998). Chiodini and Marini (1998) initially estimated an equilibrium temperature of 200–240 °C for the vapour-dominated gas equilibration zone underneath BG. Successively, Caliro et al. (2007) demonstrated, based on isotopic ($\delta^{13}C$ of coexisting CO_2 and CH_4) and chemical (CO_2-H_2O-CH_4) information, that CH_4-based geothermometers imply equilibrium temperatures (>360 °C) much higher than those returned by fast reacting species (H_2 and CO).

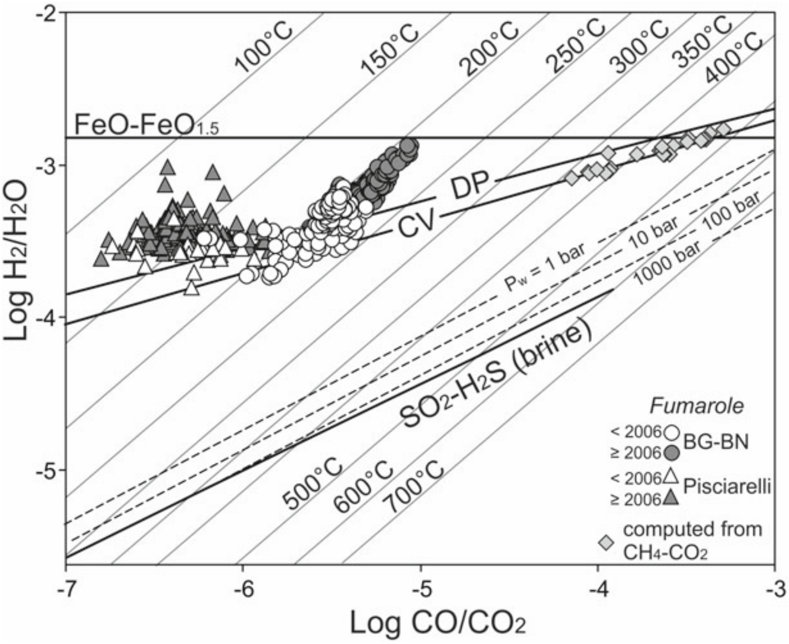
Ultimately, Caliro et al. (2007) questioned on the coupled use of species that, for kinetic reasons, equilibrate in separate zones of the hydrothermal system. Debate has also recently emerged on whether or not steam condensation (and consequent heating) takes place deep in the hydrothermal system (Moretti et al. 2017). Water removal from the gas phase, if occurring, would require reconsideration of the geothermometric-geobarometric approach (see discussion in Chiodini et al. 2015a).

In the attempt to clarify the potential role played by i) deep methane equilibration and ii) steam condensation, we here reconsider and update the log H_2/H_2O vs. log CO/CO_2 diagram (Fig. 4) originally used by Caliro et al. (2007). In the diagram, we distinguish the samples used by Caliro et al. (2007) (pre-2006 samples) from those acquired successively (post-2006 samples).

The pre-2006 Solfatara fumarole samples cluster along the theoretical composition expected from a typical hydrothermal redox buffer (D'Amore and Panichi 1980—DP redox buffer in Fig. 4, Campanian Volcanoes—CV redox buffer in Fig. 4; Chiodini and Marini 1998) at temperatures from 120 °C (Pisciarelli) to >200 °C (BG and BN). The same fumaroles also plot far from the distinctive field of high temperature "magmatic" fumaroles (SO_2-H_2S volcanic gas buffer; Giggenbach 1987). In Fig. 4, in order to illustrate the different behaviour of CH_4-based and H_2-CO-based geoindicators, we also report redox conditions (i.e., the log H_2/H_2O ratios) and equilibrium temperatures derived from CH_4-CO_2 isotopic equilibria (for those samples where carbon isotopic composition are available; Caliro et al. 2007; Bolognesi et al. 1986; Istituto Nazionale di Geofisica e Vulcanologia—Osservatorio Vesuviano unpublished data). The high temperatures estimated for these data-points ($T_{CH4\text{-}CO2}$ from 360 to 470 °C) are derived from the equilibrium carbon isotope exchange reaction between CH_4 and CO_2 (by using fractionation factors from Horita 2001). The log H_2/H_2O values are computed from the formation reaction of CH_4 from CO_2 that, expressed in terms of analytically detectable species H_2 and H_2O, is:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (1)$$

Fig. 4 Log H_2/H_2O vs Log CO/CO_2 diagram. The isotherms refer to equilibrium values for the H_2O-H_2-CO-CO_2 vapour phase. The theoretical values for redox condition typical of hydrothermal environments (FE, DP, CV) and volcanic gases (H_2S–SO_2, Giggenbach 1987) are also reported. Figure modified after Caliro et al. (2007)



Considering the dependence on temperature of the equilibrium constant of reaction 1 we can derive the following expression for the log H_2/H_2O:

$$\log H_2/H_2O = 0.25 \log CH_4/CO_2 - 0.5 \log f_{H_2O} + 2.416 - 2205.3/TK \quad (2)$$

Equation 2 is solved using (i) the analytical CH_4/CO_2 values, (ii) $TK = T_{CH4\text{-}CO2} + 273.15$, and (iii) f_{H2O} fixed by the presence of a brine ($\log f_{H2O} = 4.9–1{,}820/TK$; Giggenbach 1987). The estimated (CH_4-based) temperatures and log H_2/H_2O, plotted in Fig. 4, well illustrate the difference between the kinetically slow CH_4 and the fast-reactive species H_2 and CO: the first preserves indication on the deeper and hotter part of the system, while the latter re-equilibrate at shallower conditions upon gas ascent. It is worth noting that the CH_4-CO_2-derived temperatures and log H_2/H_2O align along the same CV and DP redox buffers that control redox conditions at near-surface (fumarolic vent) conditions (pre-2006 samples).

The post-2006 samples exhibit log H_2/H_2O ratio well above the pre-2006 samples and the theoretical ratios predicted from the DP and CV buffers. This is interpreted as due to steam condensation that has caused (since 2005–2006) the incondensable gases to increase relative to water (Chiodini et al. 2015a, b). This process, which is very efficient in heating the system, can also explain the increasing CO/CO_2 ratio (Fig. 4), the most suitable temperature geoindicator (Chiodini and Marini 1998). The recurrent episodes of condensate emission at Pisciarelli fumarole, observed since 2005–2006 (Chiodini et al. 2015a), are also direct evidence for condensation at depth.

Based on the considerations above, we estimate T-P of the shallowest part of the hydrothermal system from the functions listed in Table 1. These relationships do not consider deeply equilibrated methane and, being based on equimolar ratios between incondensable gases (Table 1; see also Chiodini et al. 2015a, 2016, 2017b), are unaffected by secondary processes involving H_2O (water condensation and/or addition).

The method again assumes the derivation of fumarolic fluids from a gas zone containing equilibrated vapour that, during its ascent, may be affected by either water addition or condensation. According to our calculations, the equilibrium temperatures and pressures of the gas equilibration zone (redox conditions are by the DP empirical function) oscillated in the 190–220 °C and 10–30 bar ranges during 1983–2010. More recently, they exhibited a gradual increase, reaching the maximum values (temperatures of ~240 °C and pressures of ~40 bar) in 2016, at the end of the observation period (note that these trends are still ongoing). We admit that choosing the DP redox buffer is somewhat arbitrary, but we stress that use of the CV buffer would only produce a shift of the computed trends to systematic higher estimated T (and P).

5 The Conceptual Geochemical Model and the Deep Resistivity Structure of the Hydrothermal System

The geochemical interpretation of the fumarolic composition in terms of P–T-redox conditions and liquid/gas phases, the mixing between meteoric and magmatic fluids, and the measured gas fluxes, all concur to define the conceptual model of the hydrothermal system feeding the Solfatara fumaroles. Geochemical information is sketched over a 2D resistivity model of Solfatara, derived by Audio Magneto Telluric measurements, which gives a realistic picture of the geometry of the system up to a depth of 2.5 km (Fig. 5). In particular, we here refer to the Solfatara portion of a longer, recently published, 2D resistivity model (Siniscalchi et al. 2019).

The image is dominated by the presence of a ~2 km elongated vertical structure of high resistivity in axis with the Solfatara fumaroles, and with top at 300–500 m depth. This is the core of the hydrothermal structure and, in our interpretation, represents a relatively high permeability zone that allows hot fluid ascent from the deeper to the shallower portions of the

Table 1 Assumptions and functions of the geobarometric-geothermometric approach (H_2O-H_2-CO_2-CO gas system)

Assumptions
Presence of an equilibrated gas phase in the 'gas equilibration zone'
Redox conditions fixed by the rock matrix (f_{O_2}-T function of D'Amore and Panichi 1980)
Saturated vapour (i.e., P_{H_2O} fixed by liquid–vapour coexistence)
Secondary processes can affect H_2O (i.e., water addition or vapour condensation)
Geobarometric and geothermometric functions
$T = 3{,}133.5/(0.933 – \text{Log } XCO/X_{CO_2})$
$\text{Log } P_{H_2O} = 5.51 – 2{,}048/TK$
$\text{Log } P_{CO_2} = 3.025 + 201/TK – \text{Log } X_{H_2}/X_{CO}$
$P_{tot} = P_{CO_2} + P_{H_2O}$

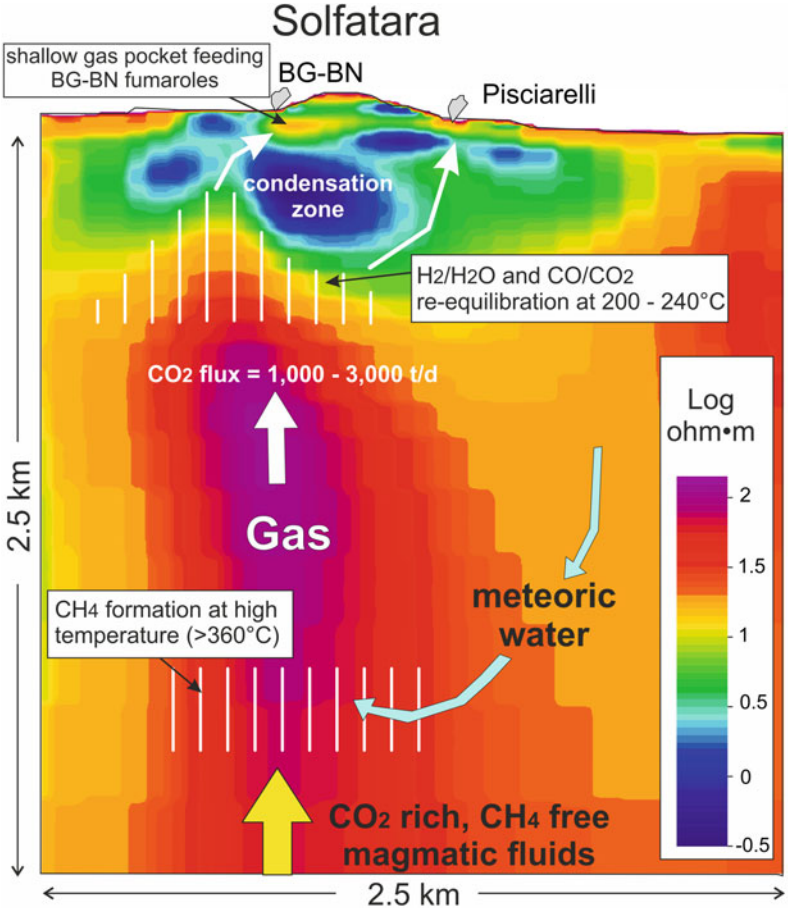


Fig. 5 Conceptual model of the hydrothermal system feeding the Solfatara fumaroles sketched over the 2D resistivity model of the Solfatara subsoil. Figure modified after Siniscalchi et al. (2019)

hydrothermal system. Relatively oxidised magmatic fluids (probably methane-free) enter the system at the bottom in a zone of very high temperature. For instance, temperatures as high as > 700 °C were recently modelled at depths of only 3–3.5 km (Amoruso et al. 2017). Here, the magmatic component mixes with and vaporises hydrothermal liquids of meteoric origin (Caliro et al. 2007), causing the more reducing redox conditions required for methane formation at the relatively high temperatures returned by the CH_4-based geoindicators ($T > 360$ °C). From that zone, the gas phase rises up to 300–500 m, where the resistive structure is interrupted by very conductive layers (cyan to blue colours), interpreted as reflecting hydrothermally altered zones (argillitic and phyllitic zones; Siniscalchi et al. 2019) and a liquid phase-dominated environment.

The upper part of the vertical permeable structure, covered by these impermeable layers, is likely the zone of H_2 and CO re-equilibration, i.e., the zone pertinent to our T-P estimations (gas equilibration zone). From that zone, the gas moves toward the surface through fractures and shallow gas pockets whose existence has been highlighted by detailed geoelectric surveys (Gresse et al. 2017, 2018). The main gas-ascent paths (white arrows in Fig. 5) connect the gas-equilibration zone directly to the gas pocket feeding the BG fumarole and, less directly, to the Pisciarelli fumaroles. It is during this transfer that condensation and/or addition of shallow waters may occur, modifying the composition of the original fluids.

6 Evolution of the Hydrothermal System During the Last 40 Years

The pulsed injection of magmatic fluids (IMF) into the hydrothermal system feeding the Solfatara fumaroles is thought to be one of the key processes that has controlled the evolution of the system during the last 40 years (see Chiodini et al. 2016 and references therein). During this time, the IMF episodes changed in frequency and intensity, ultimately causing the evident changes in degassing flux and geometry, and in the isotopic and chemical composition of the fumaroles (Fig. 6).

Chiodini et al. (2003) first demonstrated that both the large 1982–1984 bradyseismic crisis and the two mini-uplift episodes in 1989 and 1994 were followed, after some time, by evident peaks in the CO_2/H_2O ratio (Fig. 6a). Chiodini et al. (2003) were able to reproduce the shape and the timing of these peaks using a simple model that simulates the injection of a CO_2-rich gas phase (the magmatic component) into a porous media, ideally representing the hydrothermal system (see Fig. 6a and Fig. 5 in Chiodini et al. 2003).

In 2000, the pulsed behaviour of the fumarolic CO_2/H_2O ratio terminated and transitioned into a quasi-monotonic increasing trend (Fig. 6a). This led the fumarolic CO_2/H_2O ratio to increase from 0.15 to 0.18 in 2000 to ~0.4 in 2018–2019 (Fig. 6a). This large change has been interpreted as due to the combined action of (i) partial steam condensation, induced by the pressurisation of the system, (ii) CO_2 addition from decarbonation of hydrothermal calcite (Chiodini et al. 2015b), favoured by the heating of the system, and (iii) more frequent IMF events. That IMF events have frequently occurred in the last 20 years is testified by the recurrent peaks of the CO_2/CH_4 and He/CH_4 ratios (Fig. 6b; Chiodini 2009; Chiodini et al. 2012, 2015a, 2016).

Any magmatic fluid input at the base of the hydrothermal system causes, in fact, an increase of magmatic species such as CO_2 (and He) relative to CH_4, this latter being typically formed in hydrothermal environment (Chiodini 2009). These geochemically inferred IMF events are independently supported by seismicity clusters and pulsed deformations occurring few hundred days before the degassing anomaly is detected in the fumaroles (Fig. 7). Another key aspect to understand the 1990–2018 evolution of the CFc is the continuous decrease of the fumarolic N_2/He ratio (Fig. 6c). Considering the prevalent magmatic origin of both N_2 and He, and that the former (N_2) is the least soluble in primitive Campi Flegrei magmas, Caliro et al. (2014) interpreted the decreasing N_2/He ratios as caused by upward migration (lower pressure) of the gas–melt separation zone. Chiodini et al (2016) additionally argued that a lower magma degassing pressure would have resulted into a progressively more H_2O-rich magmatic gas phase, ultimately leading to the heating and

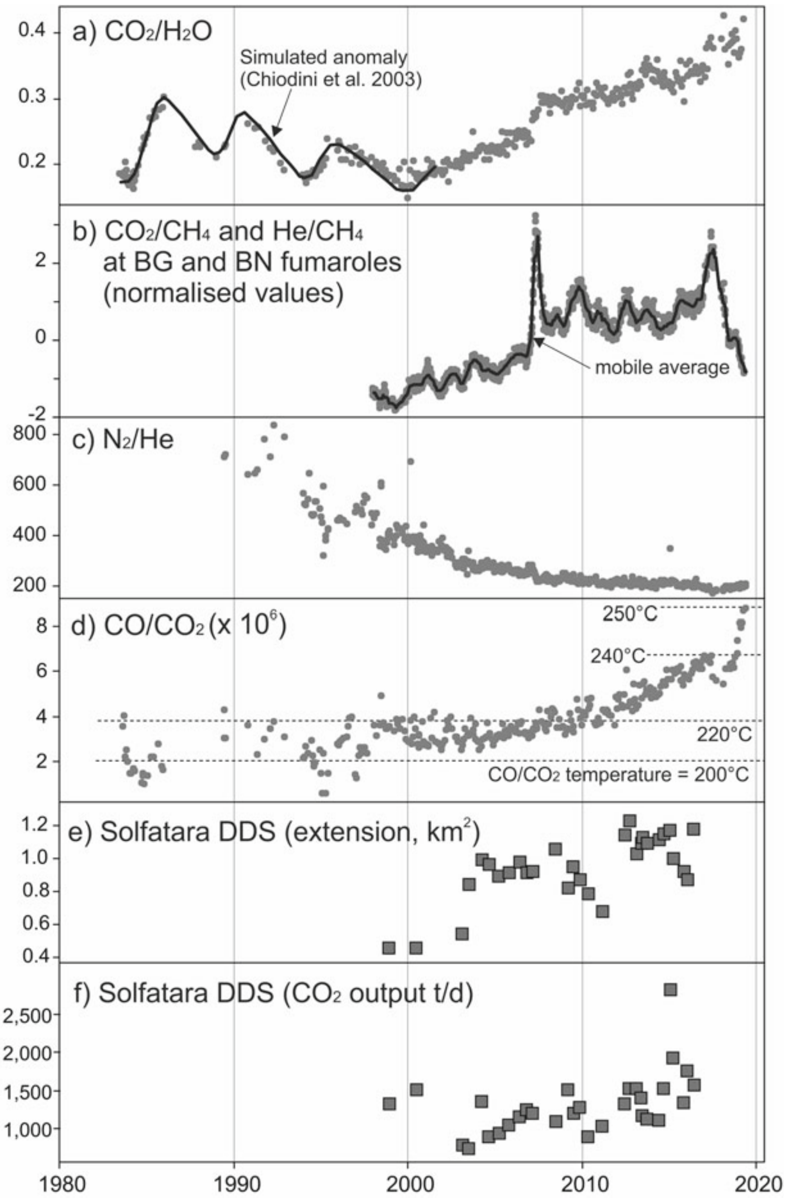
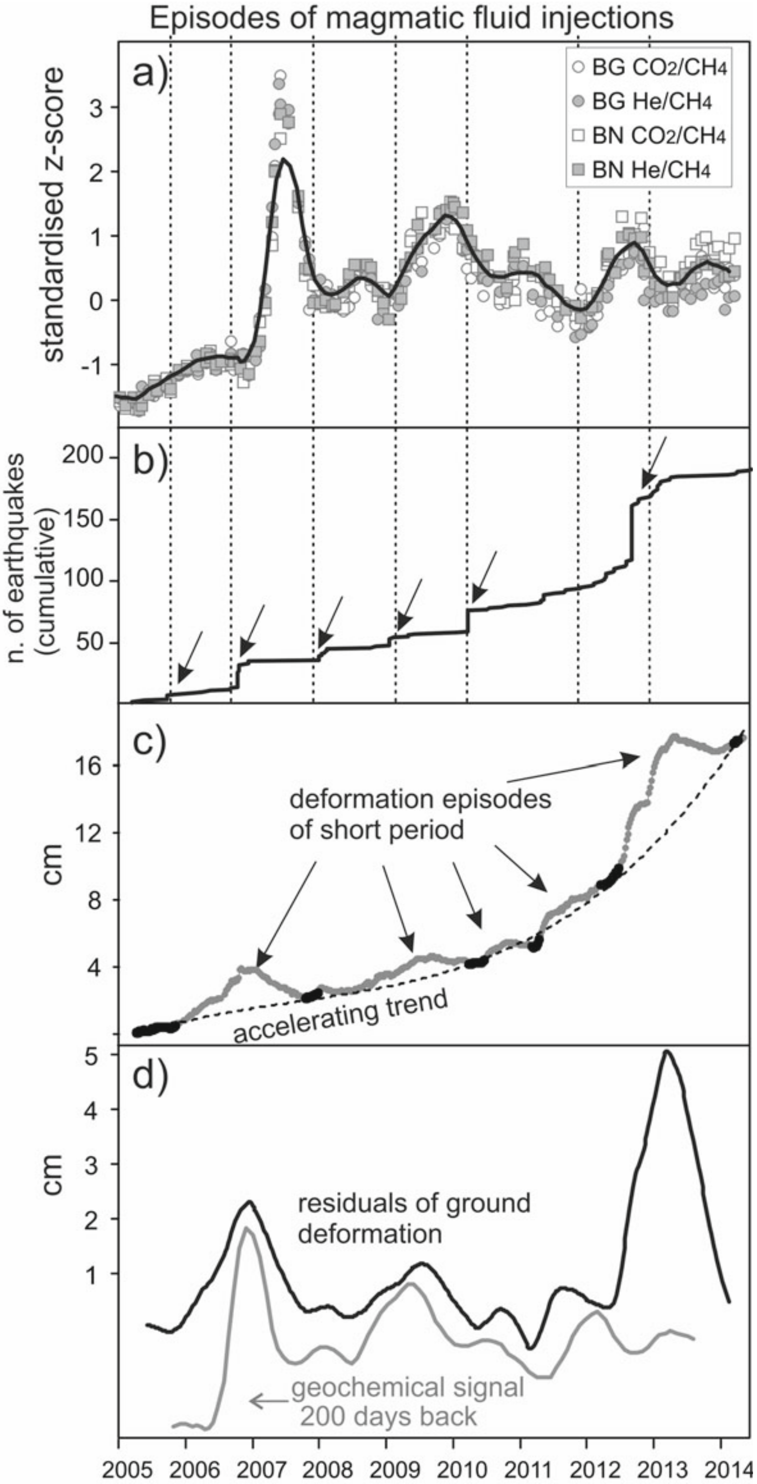


Fig. 6 Chronograms of different parameters in the 1983–2019 period. **a** CO_2/H_2O ratio. The dark grey line represents the values simulated by injecting CO_2 rich magmatic fluid at the base of the hydrothermal system (Chiodini et al. 2003). **b** CH_4 based geoindicators of magmatic fluids (Chiodini 2009). In order to compare the different signals, the measured data were normalised (standardised z-score) by removing the mean and dividing by their standard deviation (1998–2018 period). **c** N_2/He ratio (Caliro et al. 2014); **d** CO/CO_2 ratio. The isotherms refer to the CO-CO_2 temperatures (see Table 1); **e** extension of the Solfatara DDS; **f** CO_2 output from the Solfatara DDS (Cardellini et al. 2017). Figure modified after Chiodini (2009), Chiodini et al. (2003), Caliro et al. (2014), Cardellini et al. (2017)

pressurisation of the hydrothermal system. This is in line with results returned by fumarolic gas geoindicator for the last period of observation (e.g., CO/CO_2 ratio and temperature estimations in Fig. 6d, pressure estimations in Fig. 8d).

As noted above (cfr. Sect. 2), the post-2000 period has also been characterised by an enlargement of the Solfatara DDS, and by a remarkable increase of its CO_2 output. It is worth noting that, in addition to the DDS structure, CO_2 is also vigorously released by the fumarolic vents, especially at Pisciarelli (Aiuppa et al. 2013). At Pisciarelli, the main vent (Soffione) has shown a factor > 3 increase in CO_2 discharge since 2012, reaching in 2018–2019 levels (500–600 tons/day) that are similar to the CO_2 flux associated to medium-sized erupting arc volcanoes (Fig. 8d; Tamburello et al. 2019).

Fig. 7 **a** Geochemical signals; **b** cumulative number of Campi Flegrei earthquakes, and **c** deformation path (baseline length variation between the GPS stations ACAE and ARFE). **d** comparison of the residual of ground deformation path with respect to a polynomial fit with the geochemical signal. Figure modified after Chiodini et al. (2015a)



7 Conclusive Remarks

We have reviewed here the current state-of-the-art in our understanding of the CFc hydrothermal setting and behaviour. The emerging scenario is that of a very dynamic, rapidly evolving hydrothermal system. Results strongly suggest that the ongoing (since 2000) CFc unrest is triggered by a degassing magma source, but also that the system's response is strongly modulated by dynamics and structures of the overlying hydrothermal envelope (Fig. 8). The vertical displacement time-series (Fig. 8a, maximum values measured at RITE GPS station) clearly point to ongoing uplift since the first years of this millennium. Of particular relevance has been the 2012–2013 crises, during which ground deformation approached a power-law growth rate (red arrow in Fig. 8a), a fact that (with other concurrently observed signals) contributed to the

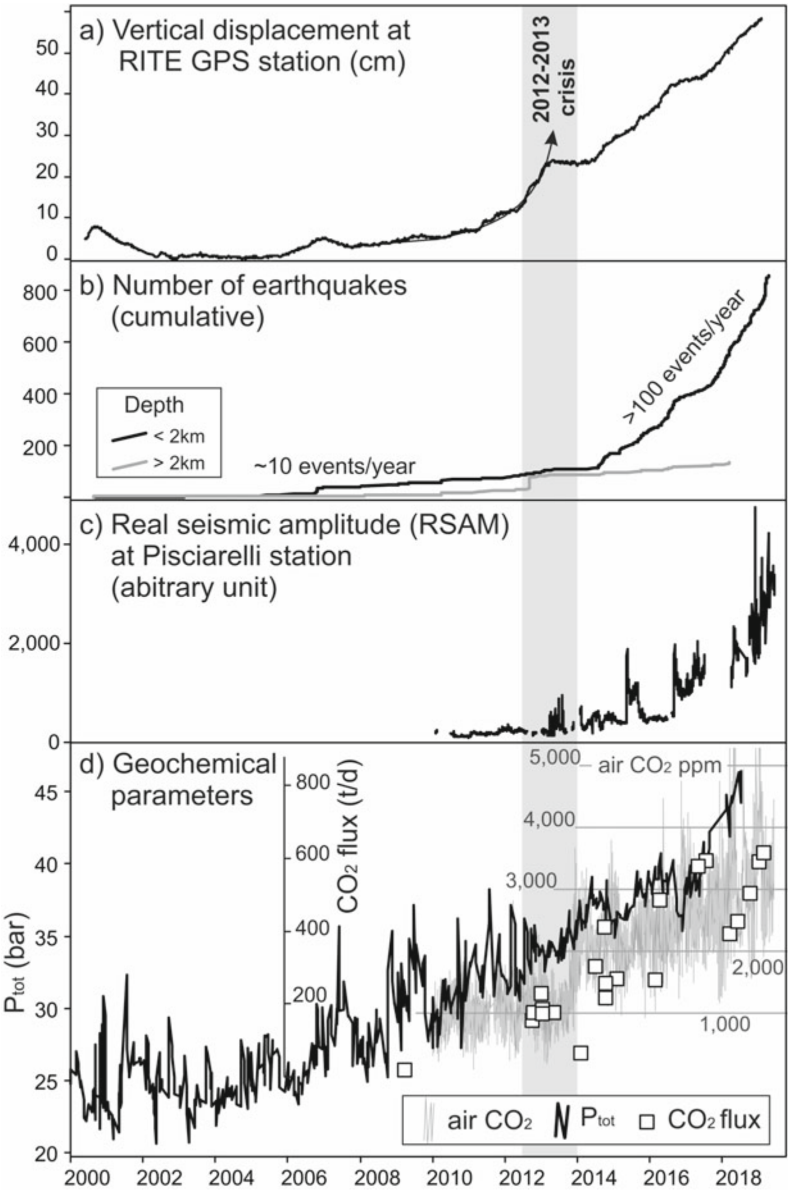


Fig. 8 Geophysical and geochemical signals at the Campi Flegrei caldera in the 2000–2019 period (modified after Giudicepietro et al. 2019). **a** Maximum vertical displacement at CFc (Tamburello et al. 2019); **b** Number of earthquakes (Giudicepietro et al. 2019). Shallower earthquakes (depth < 2 km) clustered in an area of few km^2 centred at Solfatara; **c** RSAM registered by the Pisciarelli seismic station (Chiodini et al. 2017a; Giudicepietro et al. 2019); **d** Geochemical parameters include: fluid pressure estimated at the Solfatara fumaroles (see Table 1), CO_2 fluxes measured at Pisciarelli vent (Tamburello et al. 2019; Aiuppa et al. 2015), air CO_2 concentration (grey line) automatically measured by a station sited at Pisciarelli (Tamburello et al. 2019)

decision taken by the Italian Dipartimento di Protezione Civile of raising the CFc alert level from green (quiet) to yellow (attention). The 2012–2013 crisis fortunately did not culminate into an eruption, yet may have represented a turning point in the unrest. In 2014, the number of shallow earthquakes (i.e., within the hydrothermal system feeding the Solfatara manifestation) has increased by a factor > 10 (Fig. 8b, Giudicepietro et al. 2019), concurrently with unequivocal signs of escalating hydrothermal activity (Fig. 6c, d). At Pisciarelli, the fumarolic CO_2 output has grown by a factor of 3 in only a few years (Fig. 8d). This increasing CO_2 degassing has been paralleled by strikingly similar temporal evolutions of (i) fluid pressure (Fig. 8d), (ii) air CO_2 concentrations in the surroundings of the vent (Tamburello et al. 2019; Chiodini et al. 2017b), and (iii) seismic tremor sourced within the vent (Fig. 8c, d; Chiodini et al. 2017b; Giudicepietro et al. 2019). This evolution clearly requires carefully scientific scrutiny and intensified monitoring in the years to come.

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