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Evidence of thermal-driven processes triggering the 2005–2014 unrest at Campi Flegrei caldera

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ABSTRACT

An accelerating process of ground deformation that began 10 years ago is currently affecting the Campi Flegrei caldera. The deformation pattern is here explained with the overlapping of two processes: short time pulses that are caused by injection of magmatic fluids into the hydrothermal system; and a long time process of heating of the rock. The short pulses are highlighted by comparison of the residuals of ground deformation (fitted with an accelerating polynomial function) with the fumarolic CO_2/CH_4 and He/CH_4 ratios (which are good geochemical indicators of the arrival of magmatic gases). The two independent datasets show the same sequence of five peaks, with a delay of ~200 days of the geochemical signal with respect to the geodetic signal. The heating of the hydrothermal system, which parallels the long-period accelerating curve, is inferred by temperature–pressure gas geoindicators. Referring to a recent interpretation that relates variations in the fumarolic inert gas species to open system magma degassing, we infer that the heating is caused by enrichment in water of the magmatic fluids and by an increment in their flux. Heating of the rock caused by magmatic fluids can be a central factor in triggering unrest at calderas.

1. Introduction

The trigger mechanism of unrest at active calderas is one of the most problematic issues of modern volcanology (Newhall and Dzurisin, 1988; Lowenstern et al., 2006; Troise et al., 2006; Gottsmann and Marti, 2008). In particular, magma displacement *versus* hydrothermal dynamics is one of the central questions for an understanding of the signals of several restless calderas on Earth, including, e.g., Yellowstone (Wicks et al., 2006; Lowenstern et al., 2006; Dzurisin et al., 2012), Long Valley (Hill, 2006), Santorini (Parks et al., 2012), Nisyros (Chiodini et al., 2002), and Campi Flegrei. Here we focus on Campi Flegrei caldera (CFc), which is sited in the densely inhabited metropolitan area of Naples (southern Italy; Fig. 1, Napoli). Campi Flegrei caldera has recently given clear signs of potential reawakening (Chiodini et al., 2012) where long time series of geophysical and geochemical data are available. Throughout its history, CFc has alternated between phases of uplift and subsidence over a range of timescales (Rosi et al., 1983; Di Vito et al., 1999; Orsi et al., 2004; Morhange et al., 2006), and it showed evidence of decades-long inflation prior to the last magmatic eruption (the AD 1538 Monte Nuovo eruption; Dvorak and Mastrolorenzo, 1991). The Monte Nuovo eruption was followed by a long period of subsidence, until the early 1950s, when inflation was resumed. This has culminated in two major uplift and seismic episodes ('bradyseisms'), which occurred in 1969–1972 and in 1982–1984, which have shown a total vertical displacement of 3.8 ± 0.2 m (Del Gaudio et al., 2010, and references cited therein). In 1982–1984, the maximum uplift of 1.8 m was accompanied by ~16 000 shallow earthquakes that affected CFc, which caused the partial evacuation of the heavily populated town of Pozzuoli (Barberi et al., 1984).

Since 1985, CFc has been slowly subsiding, which has been interrupted by a few minor uplift events. In 2005, there was new inflation, which accelerated and reached a maximum vertical displacement of about 23 cm by June 2014. This last stage was accompanied by weak seismicity, by a strong increase in fumarolic activity (Fig. 2), and by important compositional variations in the fumarolic effluents, which were interpreted as increased contributions from a magmatic source (Chiodini et al., 2012, and references therein). For instance, these phenomena induced the Italian Civil

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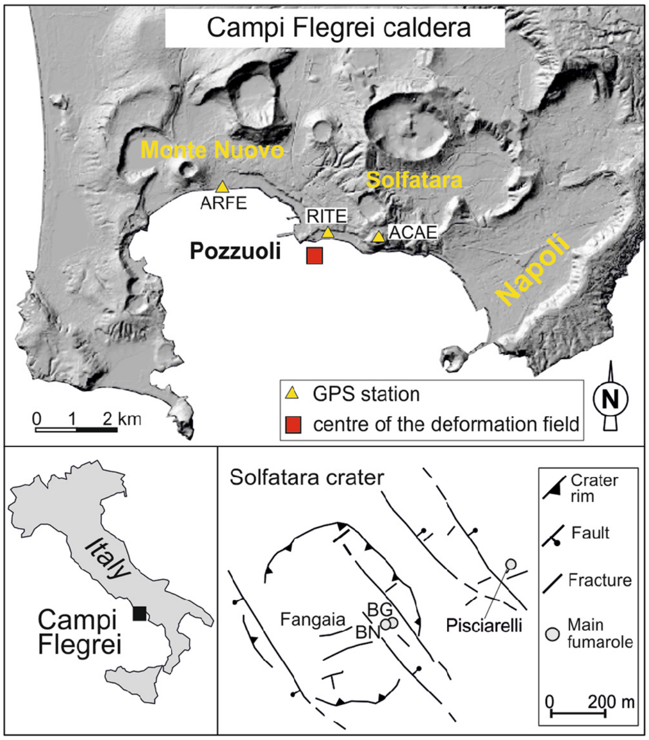

Fig. 1. Location of Campi Flegrei caldera, Solfatara crater, and the main fumaroles. The map also shows the position of the CGPS stations referred to in the text, and the deformation field during 2005–2014.

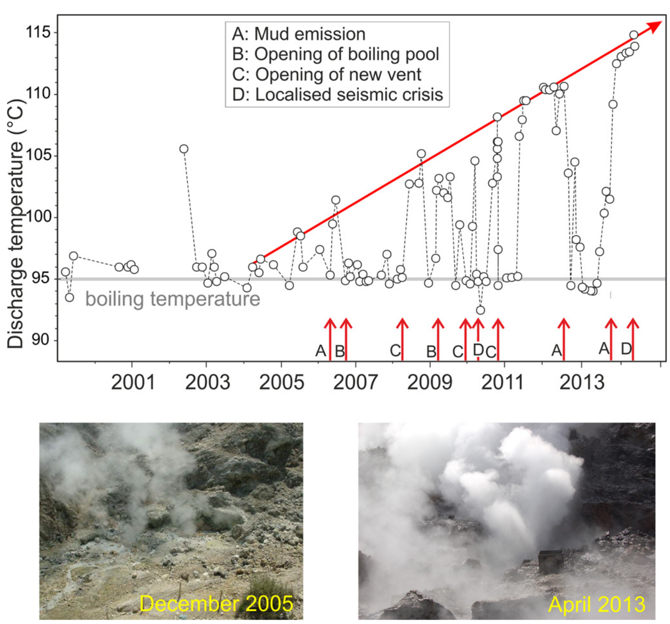

Fig. 2. Time series of discharge temperatures at Pisciarelli fumarole, and chronogram of localized phenomena that have affected the hydrothermal site (red arrow). The two pictures highlight the strong increase in fumarolic flow rate from 2005 to 2013. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Defence to change the state of Campi Flegrei from the green level (quiet) to the yellow level (scientific attention).

The first part of this study aims to illustrate the main features of this hydrothermal system. Then, we investigate the possible causes of the new unrest at CFc, by comparison of the long time series of the Solfatara fumarole composition with ground deformation data obtained from the continuous GPS network (De Martino et al., 2014).

1.1. *The hydrothermal system that feeds Solfatara*

A conceptual geochemical model of the hydrothermal system that feeds the fumaroles of Solfatara based on fumarole effluent composition was first proposed by Cioni et al. (1984), and then refined by Cioni et al. (1989), Chiodini et al. (1996, 2001, 2010), Chiodini and Marini (1998), and Caliro et al. (2007). According to the most comprehensive work of Caliro et al. (2007), hot gases separate from the magma at depth, ascend toward the surface, mix with boiling meteoric water to form a gas plume that feeds fumaroles and diffuse soil degassing at Solfatara. This geochemical interpretation has been supported by numerous physical–numerical simulations that have been published in the last 10 2years (Chiodini et al., 2003, 2012; Todesco et al., 2003; Todesco, 2009; Rinaldi et al., 2010; Petrillo et al., 2013). All of the models have consisted of injection at depth beneath Solfatara crater (1.5–2.5 km) of a hot CO_2–water mixture, where its flux is constrained by the surface hydrothermal flux measured at Solfatara. All of the simulations have been performed with the TOUGH2 code (Pruess, 1991) under steady-state conditions, and they have returned the presence of a gas plume that vertically connects the deep injection zone to the surface.

Together with geochemical interpretations and simulation results, other independent data highlight the presence of a gas plume in the subsoil of Solfatara crater:

- The total CO_2 release from diffuse degassing processes at Solfatara and its surroundings ($\sim$1.4 km^2; Fig. 3a) was estimated at 1000 t/d to 1500 t/d from 1998 to 2010 (Chiodini et al., 2010). In addition, recent measurements of gas flux from the three main fumaroles of Solfatara that were performed in January 2013 indicated a total CO_2 output of up to $\sim$600 t/d (Aiuppa et al., 2013). The total CO_2 flux of 1500 t/d to 2000 t/d was obtained by summing the fumarole fluxes and the diffuse emission, and this has to be considered as a minimum estimation of the total hydrothermal CO_2 output, because it does not consider the flux of the numerous smaller fumarolic discharges that have never been measured. Such high hydrothermal CO_2 flux is more compatible with the presence in the subsoil of a large zone where there is a gas phase (i.e., the gas plume), rather than with a boiling process of a liquid, which would require unreasonable amounts of boiling water. For example, at Yellowstone, high diffuse CO_2 fluxes of the same magnitude as at Solfatara (i.e., $\sim$kg m^{-2} d^{-1}), are normally found in vapor-dominated hydrothermal areas (i.e., acid–sulfate areas), while relatively low diffuse CO_2 fluxes are observed in areas that are dominated by thermal liquid discharges (e.g., alkaline-chloride areas) (Werner and Brantley, 2003).
- At Solfatara, the aquifer is anomalously high for both the water table height (Fig. 3b) and the water temperature (Fig. 3c), with temperatures up to boiling point (Petrillo et al., 2013). These anomalies are due to the large amounts of condensates, which are of the order of thousands of tons per day, and which locally recharge and heat the groundwater system (Bruno et al., 2007; Petrillo et al., 2013). The height of the water level indicates that a pressurized gas plume sustains the aquifer here. Similar observations of aquifers saturated with hot water condensing from an underlying gas reservoir have been reported for vapor-saturated hydrothermal systems in Yellowstone (Zohdy et al., 1973) and at Waimangu, New Zealand (Legaz et al., 2009).
- The S-wave seismic velocity (*Vs*) models (data from Battaglia et al., 2008; Zollo et al., 2006; Fig. 3d) clearly delineate a vertical, roughly cylindrical, high-*Vs* structure that extends from the surface close to Solfatara crater, down to at least 1.5 km. This *Vs* anomaly is unique in the shallower part of CFc, and

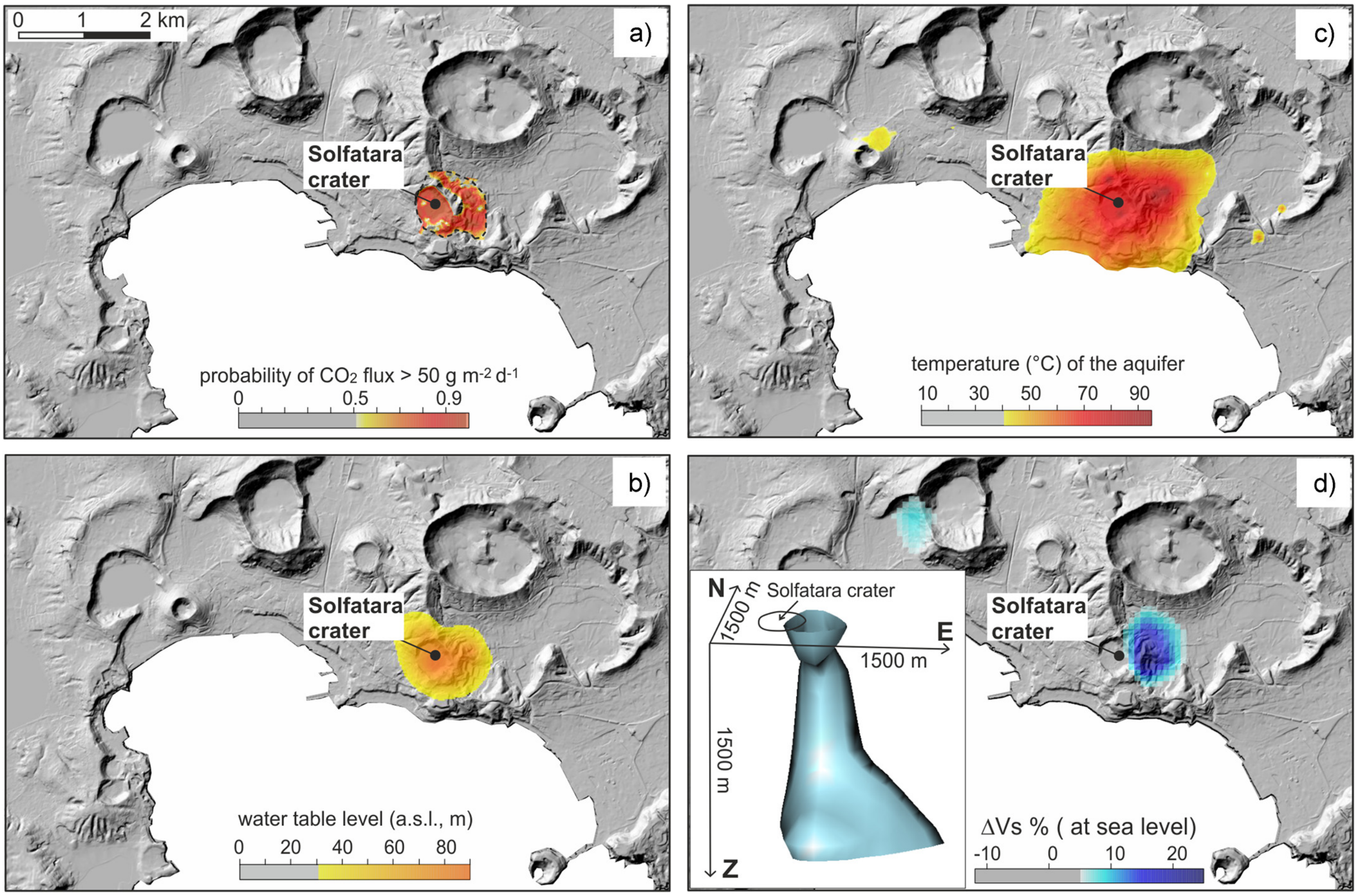

Fig. 3. Main anomalies that characterize Solfatara crater and its surroundings: (a) soil-diffuse fluxes of CO_2; (b) height of the water table; (c) groundwater temperatures; and (d) anomalies in *Vs* velocities at sea level. The anomalies refer to the percent variations with respect to the mean value at each depth. The inset in (d) shows the volume containing anomalies of greater than 18%. The spatial coincidence among the different anomalies is caused by the presence of a gas plume in the subsoil of the area.

it can be attributed to the presence of gas instead of liquid, as suggested by laboratory measurements of *Vs* in dry samples of CFc tuffs, which are systematically 10% to 50% higher than the same samples saturated with liquid (Giberti et al., 2006). This vertical structure (Fig. 3d, inset) represents an easy way to transfer up-flowing hydrothermal gases that cause the evident surface anomalies in the gas flux, temperature and water-table level. The deep source of this hydrothermal gas plume might be the area of anomalously low *Vp*/*Vs* ratio, the roof of which is located 4 km below the city of Pozzuoli, which has been interpreted as a high fluid-compressibility (gas-saturated) rock formation (Vanorio et al., 2005).

– The geodetic imaging of InSAR data (D'Auria et al., 2012) reveals that during the 2006–2007 uplift episode, the ground deformation source below the Solfatara–Pisciarelli area had a roughly cylindrical shape, with a height of about 2 km and a radius of about 200 m. This source inflated in Oct. 2006, and deflated at the end of 2007. The onset of the inflation coincided with a seismic swarm of long-period events located underneath Solfatara. The inversion of the data showed the upward migration of fluid batches within this source.

In summary, the main features of the hydrothermal system that feeds the Solfatara fumaroles are illustrated in Fig. 4.

The system consists of: (i) a deep zone of gas accumulation (Fig. 4, 'magmatic gas') which is located at ∼4 km in depth (Vanorio et al., 2005), and which supplies hot gas to the system. In this zone, the presence of a small batch of magma has been hypothesized (De Siena et al., 2010); (ii) a shallower reservoir (∼2 km in depth), where magmatic fluids mix and vaporize liquid of meteoric origin that forms the Solfatara gas plume. This scheme was previously inferred from geochemical interpretations (Caliro et al., 2007, 2014; Chiodini et al., 2012), and it was also supported by the most recent inversion of the ground deformation

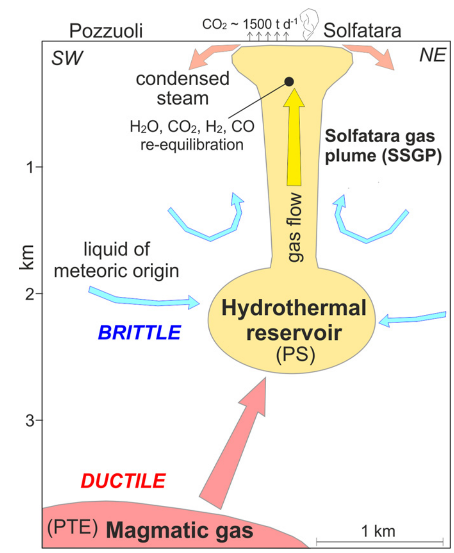

Fig. 4. Conceptual model of the hydrothermal system feeding the Solfatara fumaroles. PTE and pressurized spheroid (PS) refer to the sources of the ground deformation that is active at CFc, according to Amoruso et al. (2014a, 2014b).

data for the 1982–2013 period (Amoruso et al., 2014a, 2014b). The observed deformation would be controlled by pressure changes in two distinct sources: a pressurized triaxial ellipsoid (PTE), oriented NW–SE and centred at about 4 km in depth below Pozzuoli; and a pressurized spheroid (PS) located at ∼2 km in depth below Solfatara crater. The PTE and PS are coincident with the deeper and shallower parts of the hydrothermal system (Fig. 4).

2. Materials and methods

2.1. Datasets used

In the following sections we will mainly refer to:

- The composition of the Solfatara fumaroles (BG 161 °C ± 2.7 °C; BN 146.0 ± 2.0 °C, Fig. 1), which are sampled monthly and analyzed in the framework of the volcanic surveillance of CFc. The chemical species routinely determined are H_2O, CO_2, H_2S, H_2, N_2, CH_4, He and CO (in order of decreasing concentrations), which have shown large compositional variations over time (Chiodini et al., 2010). The entire dataset, which consists of 446 previously published samples and 83 new samples, analytical methods, and errors accompany this study, in the electronic Annex.
- The dataset of the CFc surface deformation detected by continuous GPS stations (CGPS), as recently published in an open-access database (De Martino et al., 2014).
- The vertical maximum displacement recorded by high-precision leveling surveys for the 1982–2003 period (Del Gaudio et al., 2010).

2.2. Gas equilibria models

In this study, we investigated the gas equilibria within the H_2O–CO_2–H_2–CO gas system, modifying the approach described in Chiodini and Marini (1998) in order both to derive gas geoindicators independent on the occurrence of condensation processes and to estimate the fraction of water removed or added in secondary processes. The equilibrium temperature and pressure were derived based on the following assumptions:

(a) The H_2 and CO fugacities are controlled by the dissociation of H_2O and CO_2 according to:

$$CO_2 = CO + \tfrac{1}{2}O_2, \quad (1)$$

$$H_2O = H_2 + \tfrac{1}{2}O_2. \quad (2)$$

(b) The equimolar ratios between the molar fractions are equal to the ratios between the fugacities ($X_i/X_j \approx f_i/f_j$), an assumption that is generally valid in the typical pressure–temperature range of hydrothermal systems.

(c) The water fugacity is fixed by the coexistence of liquid and vapor phases.

(d) The gases equilibrate in the vapor phase. This assumption is not obvious, because in most cases the fumaroles are fed by boiling liquid rather than from zones of equilibrated vapor. However, at Solfatara, there is abundant evidence for a large gas plume where reactive gas species equilibrate (see Section 2).

(e) Redox conditions are controlled for both the H_2–H_2O and CO–CO_2 couples by a unique f_{O_2}–T function. In particular, we applied the function of D'Amore and Panichi (1980) ($\log f_{O_2} = 8.20 - 23643/T$, where T is the temperature, expressed in Kelvin), which according to Chiodini and Marini (1998) is the function that generally better describes redox conditions, among the different functions proposed for hydrothermal environments.

With these assumptions, we derived the following geothermometric and geobarometric functions:

$$T = 3238/\left[1.115 - \log(CO/CO_2)\right], \quad (3)$$

$$\log P_{H_2O} = 5.510 - 2048/T \quad \text{(Giggenbach, 1980)}, \quad (4)$$

$$\log P_{CO_2} = 3.573 - \log(H_2/CO) - 46/T \quad \text{(Chiodini and Cioni, 1989)}, \quad (5)$$

where the estimated values depend on the measured ratios of the noncondensable gases (i.e., CO/CO_2 and H_2/CO).

The fraction of the water removed or added in secondary processes was computed by comparing the ratio between the equilibrium P_{H_2O} and P_{CO_2} [$(H_2O/CO_2)_{eq}$] with the analytical fumarolic ratio of H_2O/CO_2. Theoretically, these two values should be almost equal if the gas moves from the equilibration zone to the fumarolic discharge without water and CO_2 removal or addition. Assuming that CO_2 removal or addition is negligible, the H_2O and CO_2 mass balance between the equilibration zone (subscript *eq*) and the fumarolic discharge (subscript *fu*) can be expressed by the simple relations:

$$CO_{2,eq} = CO_{2,fu} \quad (6)$$

$$H_2O_{eq} = H_2O_{fu} + f\,H_2O_{eq} \quad (7)$$

where f is the fraction of the water removed (sign +, condensation) or added (sign −, addition of water) in secondary processes, and is computable. Combining this with Eqs. (1) and (2), we get:

$$f = \left[(H_2O/CO_2)_{eq} - (H_2O/CO_2)_{fu}\right]/(H_2O/CO_2)_{eq}. \quad (8)$$

3. Results and discussions

3.1. The pattern of the 2005–2014 ground deformation and geochemical signals

The CGPS data (De Martino et al., 2014) show that since 2005, the entire CFc has uplifted and expanded with spatially varying amplitudes, but following a similar accelerating process (De Martino et al., 2014: Figs. 2–4). The maximum vertical displacement was measured at the RITE CGPS station, the station that is closest to the center of the deformation field (Fig. 1); this uplifted by ∼23 cm from April 2005 to June 2014, following an accelerating trend. The same pattern has also characterized the horizontal displacement of CFc, as shown in Fig. 5a by the time series of the baseline length variations between the ACAE and ARFE CGPS stations, which have moved toward the ENE and WNW, respectively. In the following, we will rely on the ACAE–ARFE baseline time series, as this has been less affected by atmospheric effects than the vertical time series of the RITE station. Inspection of the curve shown in Fig. 5a suggests that there has been overlapping of a general trend of expansion with short periods of dilatation pulses (or uplifting), two of which were particularly intense and which commenced in 2006 and 2012. To derive a general long-term trend of the deformation, we fitted the CGPS measurements to a third-order polynomial equation applied to the points less affected by these pulses (i.e., the relative minima of the curve; Fig. 5a, black dots). The residuals of the observed data with respect to the curve fitting clearly show the two anomalous mini-uplift episodes of 2006–2007 and 2012–2013, along with a series of less-intense ground-deformation episodes. On the whole, the residuals

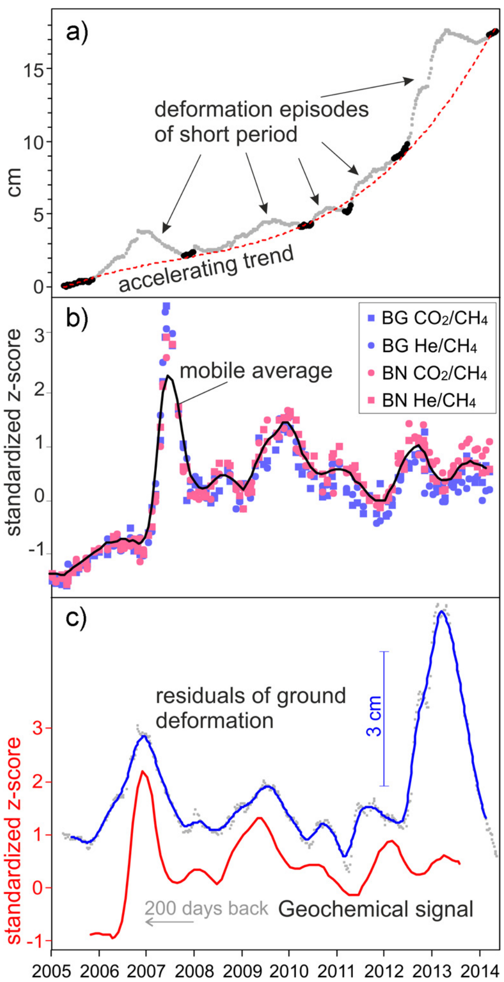

Fig. 5. Comparison between ground deformation and geochemical signals. a) 2005–2014 baseline length variation between the ACAE and ARFE CGPS stations (gray dots, see Fig. 1 for the location of ACAE and ARFE). The data used for the derivation of the 'accelerating trend' curve are reported as black dots (see the text for further explanations); b) measured CO_2/CH_4 and He/CH_4 ratios at fumaroles BG and BN. In order to compare the different signals the measured data were normalized (standardized z-score) by removing the mean and dividing by their standard deviation (2004–2014 period). The 4 months mobile average of all the geochemical data (red curve) shifted backwards by 200 days is compared in panel (c) with the 4 months mobile average of the ground displacement residual (see panel a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the deformation closely resemble the geochemical data collected at Solfatara fumaroles (Fig. 5b, c).

At the Solfatara fumaroles, the sharp increase in the proportion of the magmatic component over relatively short periods, i.e., of a few months to a year, was interpreted as resulting from magmatic fluid injections into the hydrothermal system (Chiodini et al., 2012). During these episodes, the CH_4 content of the fumaroles decreased, due to the low CH_4 content of the magmatic fluids, and possibly also because the relatively high and transient oxidizing conditions during magmatic fluid injection can prevent the formation of CH_4 in the hydrothermal environment (Chiodini, 2009). On the contrary, other gases of prevalent magmatic origin, such as CO_2 and He, can increase their relative contents, making their ratio with CH_4 a good indicator of an increasing proportion of the magmatic component. Therefore, the five peaks that affected the CO_2/CH_4 and He/CH_4 ratios of BG and BN fumaroles in 2007, 2008, 2009–2010, 2011, 2012 (Fig. 5b), which were each of about 1 year in duration, correspond to periods of magmatic fluid enrichment in the Solfatara fumaroles. These geochemical pulses closely repeat

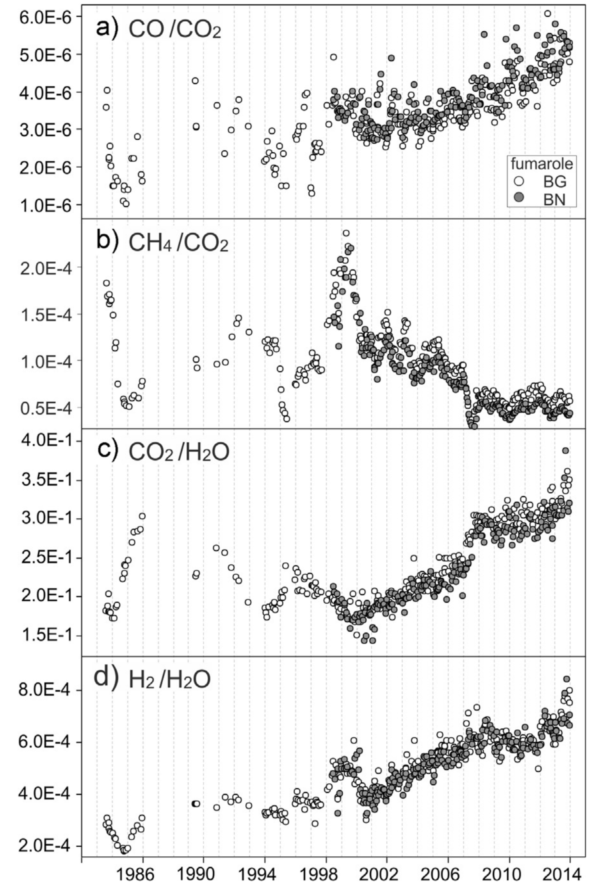

Fig. 6. Time series of (a) CO/CO_2, (b) CH_4/CO_2, (c) CO_2/H_2O, and (d) H_2/H_2O molar ratios at the Bocca Grande (BG) and Bocca Nuova (BN) fumaroles.

the same sequence of six minima and five maxima that are highlighted by the residuals of the displacements, the main difference being a time lag of about 200 days between the ground deformation and the geochemical signals (Fig. 5c).

Excluding an improbable fortuity, this correlation between two truly independent datasets can be explained by episodes of pressurization in the deeper parts of the hydrothermal system, followed by pulsed inputs of magmatic fluids into the system that feeds the Solfatara fumaroles. The delay between the two signals would represent the transfer time of the magmatic fluids from the input zone (i.e., Fig. 4, PTE reservoir) to the fumarolic discharge areas. Only the last important deformation event (Fig. 5c, 2012–2013) does not correspond to a geochemical peak of comparable intensity. It is worth noting that at that time (i.e., autumn 2012) the earthquakes hypocenters moved from below Solfatara (at a depth of ∼1–2 km) to 2 km to the west, at greater depths (2–4 km), which would suggest that a similar fluid transfer process affected another zone of CFc.

These evident episodes of gas pressurization and magmatic fluid transfer occur concurrently with the accelerating trend of deformation (Fig. 5a) the origin of which is discussed in the next sections.

3.2. Evidence of heating of the Solfatara hydrothermal system during 2005–2014

During the 2005–2014 period of accelerating deformation (Fig. 5), the CO/CO_2 ratio of the main fumaroles also showed a clear increase, from $\sim 3 \times 10^{-6}$ in 2005, to $\sim 5 \times 10^{-6}$ in 2014 (Fig. 6a). This similarity between the ground deformation and the CO/CO_2 ratio is relevant because CO is the most sensitive species to temperature among all of the fumarolic reactive gas species

(Chiodini and Marini, 1998). Due to its relatively fast kinetics for equilibration with CO_2 (Chiodini and Marini, 1998), the CO increase would appear to be caused by heating of the shallower parts of the Solfatara gas plume (Fig. 4). For the same period, the CH_4, which is a much slower species to react (Giggenbach, 1997) and which is formed in deeper parts of the hydrothermal system (Caliro et al., 2007), shows a clear general decreasing trend (Fig. 6b, CH_4/CO_2 ratio) that can be explained by the ingress of oxidizing magmatic fluids into the deeper parts of the hydrothermal system and, in turn, by a temperature increase that hinders CH_4 formation. Therefore, CO and CH_4 qualitatively indicate a temperature increase for the entire CFc hydrothermal system.

This heating of the system appears to be caused by the increment in the flux of the magmatic fluids that enter the hydrothermal system, which results in the pulsed anomalies depicted in Fig. 5c. In particular, Chiodini et al. (2012) estimated that the total injected fluid masses associated with each of these events are of the same order of magnitude (Mega ton) as those emitted during small to medium-sized volcanic eruptions, and that their cumulative curve highlights increasing activity during the period of accelerating deformation. According to the results of physical simulations (Todesco, 2009), the increment in the flux of the deep hot fluids would cause water vapor condensation within and at the border of the gas plume, and in turn, heating of the rock by the latent heat release during condensation.

The condensation of the steam might be one of the main causes of the continuous increase in noncondensable gases in fumaroles (e.g., Fig. 6c, CO_2/H_2O ratio), a process that has been of particular note in recent years. The occurrence of an ongoing process of condensation-induced heating is also suggested by repeated episodes of mud emissions, and by the formation of boiling pools of condensates at the Pisciarelli site (Fig. 1); these started in 2004, and they have been accompanied by a progressive increase in the discharge temperature of the main vent, from 95 °C to 96 °C in 2004, to 115 °C in 2014 (Fig. 2; Chiodini et al., 2011).

The important processes of condensation at the Solfatara system are highlighted by the complex electrical resistivity structure of the first 100 m below Solfatara crater, which shows that the resistive gas bodies below the fumaroles are overlain by conductive descending bodies of liquid condensates (Byrdina et al., 2014). Furthermore, the electrical resistivity image shows an ascending column of condensates that emerge at the Fangaia site (Fig. 1), which supports the occurrence of deep processes of condensation within the buried Solfatara gas plume.

Previous studies of gas-geoindicators at Solfatara (Chiodini et al., 2011, and references therein) have assumed that the measured H_2O–CO_2–H_2–CO fumarolic concentrations are fully representative of their equilibrium compositions, an assumption that will not be valid if water vapor condensation is occurring. To derive gas-geoindicators of the temperatures and pressures based on the ratios among the noncondensable gas species, which are consequently not affected by the occurrence of steam condensation, we now select as an alternative constraint the redox conditions that are fixed by a typical hydrothermal buffer. This revised method (see Section 3.2) allows the estimation of the temperatures and the fractions of the water (f) removed or added in secondary processes, such as condensation or addition of water during the transfer of the vapor from the equilibration zone to the fumaroles.

When this method is applied to the entire dataset of the BG and BN fumaroles, i.e., from 1983 to 2014, the temperature estimations (Fig. 7a) range from 190 °C to 240 °C, and they show a continuous increasing trend during the 2005–2014 phase of ground acceleration. During this last period, the temperature increased by ∼15 °C, from 217 °C ± 3 °C in 2003–2004, to 232 °C ± 2 °C in 2013–2014.

The estimated f values increase with time, in agreement with the heating of the system (Fig. 7b). Both the estimated temperatures and f have a marked negative anomaly during the 1983–1984 seismic crisis, when ∼16 000 earthquakes occurred at CFc (Fig. 7c). These anomalies might have been caused by more oxidizing conditions in the gas equilibration zone during the crisis, in which case the estimated temperature and f values would not have a physical meaning because we assumed redox conditions fixed by a hydrothermal buffer. Alternatively, they might have been caused by a real temperature decrease as a result of the input of liquid water in the Solfatara plume. This second scenario is more likely, because the thousands of earthquakes that occurred in 1983–1984, which were generally located close to Solfatara, would increase the rock permeability by creating new fractures, thus promoting seepage of colder surface waters into the hydrothermal reservoir, and its subsequent cooling. In the following period, from 1985 to 2003, the f values are scattered around 0, with most of the temperatures ranging from 200 °C to 220 °C. After 2003, and to date (2014), the computed f values show systematic positive values that indicate water removal by the condensation and heating of the system.

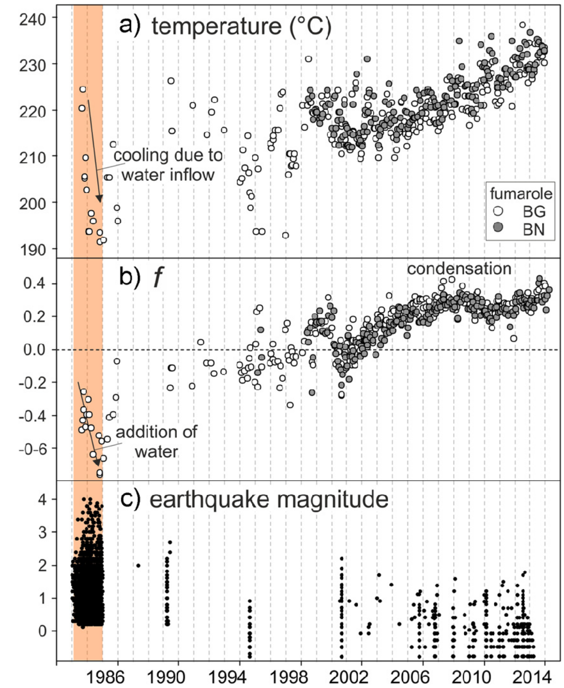

Fig. 7. Temperature (a) and f values (b) inferred from thermodynamic computations within the H_2O–H_2–CO_2–CO gas system. The variable f refers to the fraction of the water removed (sign +) or added (sign −) during the transfer of the gas from the equilibration zone to the fumarole. Earthquake magnitudes are reported for comparison in (c) (data from D'Auria et al., 2011).

The estimated f values (Fig. 7b) show the same temporal pattern as the H_2 analytical values (Fig. 6d). This is not surprising, because the selection of fixed redox conditions imposes that the H_2/H_2O ratio is a function only of temperature, and deviations from equilibrium values are interpreted as removal (or addition) of water. If we do not assume the redox constraint but, e.g., that the measured H_2O is representative of the equilibrium values, we would estimate redox conditions that would become progressively more reducing over time, which is not in agreement with the observed progressive decrease in CH_4 (Fig. 6b); this instead suggests the input of increasing amounts of oxidizing magmatic fluids in the deeper and hotter parts of the hydrothermal system.

3.3. Origin of the thermal anomaly

A first cause of the heating of the system would be the above-described increment in the flux of magmatic fluids that enter the

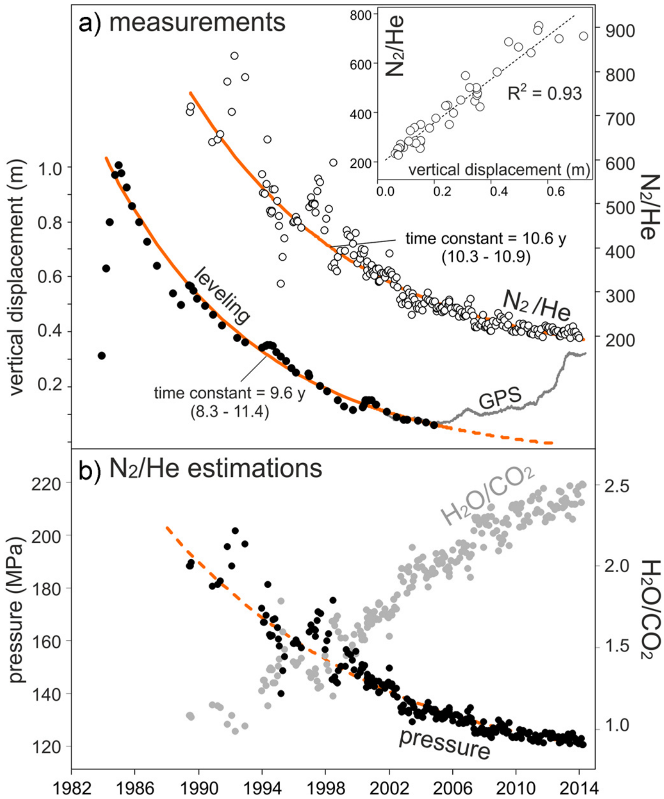

Fig. 8. Geochemical indicators and ground deformation between 1982 and 2014. (a) Measured N_2/He ratio (BG fumarole) and maximum vertical ground displacement measured at CFc by optical leveling (black dots) and CGPS (data from Del Gaudio et al., 2010; De Martino et al., 2014). The exponential decay curve of the vertical height refers to the leveling data from 1985 to 2004. Inset: the N_2/He ratio plotted against the maximum height registered 900 days before. (b) H_2O/CO_2 ratio and pressure simulated for magmatic fluids released during an open-system degassing process (inferred from the measured N_2/He fumarolic ratios, see text).

hydrothermal system (Chiodini et al., 2012). Here, we investigate the changes in the H_2O/CO_2 ratio of the fluids released by the magma, as another possible cause of the 2005–2014 period of thermal anomaly. We have made use of the results of a recent study (Caliro et al., 2014) that used variations in the ratios among the most inert gas species measured at the Solfatara fumaroles (i.e., N_2, He, CO_2) to infer the main parameters (e.g., type of magma, pressure) that control the magma degassing processes from which these species mainly originate. The experimental data were compared with those simulated for a magma-degassing model of an isothermal open system involving (at different pressures: 100 to 300 MPa) the main types of melt compositions of CFc (i.e., trachybasalt, shoshonite, tephri-phonolite, trachyte). The results of this study show that the decrease in the pressure that governs the degassing of trachybasaltic magma might well explain the observed trends, and in particular, the decrease of the N_2/He ratio because N_2 has a solubility that is lower than He (Caliro et al., 2014).

The N_2/He ratio changed from 800 in 1989, when the analysis of He was started, to ∼200 in 2012–2014, showing a spectacular decreasing trend that is similar to that of the deflation during 1985–2004 (Fig. 8a). To estimate the correlation between these two processes, the data were fitted to an exponential decay model using the least absolute residual method. The results show that the time constants of the two trends are the same at the 95% confidence interval (10.3–10.6 years, 8.3–11.4 years, for the N_2/He and deformation, respectively). This co-incidence supports the concept of a common process to explain the observed variations. The process is most likely the depressurization of the deep parts of the systems, as concluded from recent independent studies of the geodetic and geochemical data. According to Amoruso et al. (2014a), the 1985–2004 deflation of CFc was due to a pressure decrease within a stationary deformation source (i.e., Fig. 4, PTE), while the N_2/He trend has been explained by a depressurizing magma degassing process (Caliro et al., 2014).

It is worth noting that the highest correlation between the geochemical signal and the ground deformation was found by moving the N_2/He ratio back by 900 days (Fig. 8a, inset), a delay that is larger than that estimated for the CH_4-based geoindicators (i.e., ∼200 days; see above), which indicates that the N_2/He ratio is controlled by a process that occurs below the hydrothermal system, and which furnishes another independent clue as to the magmatic origin of the signal.

From each measurement of the N_2/He ratio, we computed the corresponding pressure and H_2O/CO_2 ratio of the gas released from the magma (Fig. 8b), by comparison of the observed values with the data simulated in Caliro et al. (2014). Among the different models, we chose simulation with a H_2O/CO_2 molar ratio of 1 in the first separated gas phase, and an initial pressure of 200 MPa (see Caliro et al., 2014, for further details). Note that this arbitrary choice of the initial conditions, which for instance would roughly correspond to a depth of ∼8 km assuming lithostatic control of the fluid pressure, affects the absolute values of the pressure and the H_2O/CO_2 ratio, but does not significantly affect the inferred degassing trends, because these mainly depend on the different solubilities of the gas species in the trachybasaltic melt. Inspection of the chronogram (Fig. 8b) shows that the magma degassing pressure would have decreased from 200 MPa to 120 MPa following an exponential decay trend, which matches well with an overpressure relaxation scenario; i.e., the system reached the maximum overpressure during the 1982–1984 crisis, and since that time, it has tended to a baric equilibrium condition with the confining pressure.

Based on the mutual relationship between the ground deformation and the pressure of the magma degassing (Fig. 8), we hypothesize a top-down process of depressurization of the magmatic system that is possibly controlled by the permeability of the cover of the PTE, through which the pressure excess is released by fluid transfer to the shallower parts of CFc.

The correlation between the ground deformation and the N_2/He ratio, and the derived pressure trend of the magma degassing process, disappeared during the 2005–2014 period of accelerating uplift and heating of the system. It is worth noting that the magmatic fluids would have become progressively richer in steam concurrent with the depressurization, as indicated by the simulated H_2O/CO_2 ratio that almost doubled from 2000 (Fig. 8b). Steam has a much higher enthalpy than CO_2, and this energy can be transferred easily to the rock through condensation, to contribute to rock deformation.

3.4. Heating of the system and ground deformations

Considering the measured flux of CO_2 as constant ($FLUX_{CO_2}$ ∼1500 t/d), the total amount of steam that was condensed from 2003 to 2014 in the shallower part of the Solfatara gas plume (Fig. 4) was $\sim 3.5 \times 10^9$ kg, as result of the product $FLUX_{CO_2} \times f \times (H_2O/CO_2)_{eq}$, integrated over the entire period. The corresponding total amount of heat released by this condensation was $\sim 6.2 \times 10^{12}$ kJ (i.e., with the latent heat of the steam condensation of ∼1840 kJ/kg at the estimated average temperature of ∼225 °C). This is an appreciable amount of energy, which would produce a 5 °C heat increase in a mass of $\sim 1.25 \times 10^{12}$ kg of rock, which corresponds to a volume of 0.625 km^3 (with a density of 2000 kg/m^3). On the assumption of a volumetric expansion coefficient of 30×10^{-6}/°C, the corresponding volume increase would be of $\sim 0.94 \times 10^5$ m^3; i.e., of the same order of magnitude as the volumetric expansion computed from ground deformation data by Amoruso et al. (2014b) for the shallower deformation source (PS in Fig. 4) for the period 2006–2013.

Similar, and possibly more intense, processes of heating, condensation and rock deformation will affect the deeper parts of the hydrothermal system, and probably also the magmatic gas zone (Fig. 4). Furthermore the effect of heating on ground deformation should be larger than that associated with the sole thermal expansion as suggested by the results of thermal techniques, and in particular steam injection, which are used in the oil industry for heavy-oil exploitation (e.g., Dusseault and Collins, 2008). The steam injection and the associated latent heat release will have three major effects: rock temperature increase, which in turn deforms the media through thermal expansion, thermally-induced shear dilation (Dusseault, 2011), the associated ground deformation of which is remarkably large, and enhancement of fluid-flow permeability.

At CFc, the ongoing process of heating might be one of the main causes of the 2005–2014 accelerating process of ground deformation, because: (i) the mechanical strength of the products of the shallow layers of CFc (Neapolitan Yellow Tuff) strongly decreases with thermal stressing (Heap et al., 2014), (ii) increasing amounts of magmatic gas are entering into the system (see Chiodini et al., 2012: Fig. 4c), and (iii) the magmatic gases have a progressively higher enthalpy, due to the increase in the H_2O/CO_2 ratio.

More generally, the enrichment in water with respect to CO_2 will affect the fluids released by any process of magma depressurization, because it is controlled by the different solubilities of these two species in the melt. For any caldera, either during its ascent or during a steady passive degassing period (Girona et al., 2014), the magma will depressurize and release increasing amounts of steam that will heat the system, generating signs of long duration in the deformation patterns. The repetition of such episodes and the related heating phases might be one of the mechanisms that can explain long-term unrest cycles observed at calderas. Finally, the heating might bring the system to pre-eruptive conditions causing the weakness of the rocks which cover the magma bodies.

4. Conclusions

Campi Flegrei caldera is sited in the densely inhabited metropolitan area of Naples, and over the last few decades, it has given clear signs of unrest, which have included ground deformation, earthquakes, and variations in hydrothermal activity. The last main bradyseism episode (1982–1984) was followed by slow subsidence, which was interrupted by a few minor episodes of uplift, which lasted until 2005. Then a new inflation period started with an accelerating trend, and reached maximum vertical displacement in June 2014 (of 23 cm). To investigate the causes of this new unrest at CFc, we compared long time series of fumarolic compositions that were systematically collected at Solfatara from 1983 to 2014 with the ground deformation data, with impressive correlations shown between these two independent datasets.

An important characteristic of the hydrothermal system that feeds the fumarolic activity is its vertical gas plume that is 1.5 km to 2.0 km long, for which we show for the first time an evident Vs tomographic image. This vertical plume is the shallower part of a complex hydrothermal system that is composed of a zone at $\sim$4 km in depth of magmatic gas accumulation, and a zone at $\sim$2 km in depth where magmatic gases mix with and vaporize meteoric liquid, to create the gas plume. A possible reason for the remarkable correspondence between these fumarolic compositions and the geophysical signals is the presence of this subterranean gas plume. This represents an efficient way for the transfer of fluids to the fumarolic discharges, while allowing the gas to maintain some signatures from the deeper zones of the system, the zones which are, at the same time, the sources of the CFc ground deformation.

These comparisons between the fumarolic compositions and the ground deformation suggest that two processes contribute to the ongoing CFc unrest:

1) Transient episodes of gas pressurization that are accompanied by fluid transfer from the deep magmatic gas zone to the shallower parts of the hydrothermal system, which trigger the short-term uplifting episodes;
2) A long-term process of heating of the system that causes (or contributes to) the 10-year-long pattern of accelerating ground deformation.

While the first of these processes has already been highlighted by recent investigations (Chiodini et al., 2012; D'Auria et al., 2011), the heating of the system by condensation as potentially the main factor involved in the control of the recent CFc dynamics is a possibility that has never been considered previously. The occurrence of this heating is suggested both by an evident increase in the hydrothermal activity at the surface and by the compositional variations of the fumarole gases that indicate both a temperature increase (i.e., increase in fumarolic CO and H_2, decrease in CH_4) and the occurrence of condensation processes within the hydrothermal system. The observed changes in the geochemical parameters occur simultaneously with the acceleration of the ground deformation.

The main reason for this phase of heating is an increase in the flux of magmatic steam, which following the 1983–1984 bradyseism, might have been favored by a permeability increase in the cover of the magmatic zone and by the depressurization of the deep gas reservoir. As CO_2 has lower solubility than H_2O, the magma depressurization first produced the CO_2 exsolution during the major uplift stages, which then in the following stage caused a change toward more H_2O-rich compositions of the fluids released by the magma. The H_2O transferred as steam in the hydrothermal system can efficiently deform the rock.

To date, inversion of the CFc deformation data has been based on isothermal models that have neglected the thermal induced effects, which conversely might represent one of the main processes in the recent deformation history of CFc. Coupled non-isothermal thermal-hydrologic-mechanical models, together with magma degassing simulations, and geochemical interpretation of fumarolic compositions can substantially improve our understanding of the trigger mechanisms of unrest at CFc, and in general, at any active caldera.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2015.01.012.

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