

Discriminating carbon dioxide sources during volcanic unrest: The case of Campi Flegrei caldera (Italy)

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ABSTRACT

Large calderas are among the main emitters of volcanic CO₂, which is mainly supplied by the deep degassing of magmatic fluids. However, other sources of non-magmatic CO₂ can also occur due to the intense interaction among magmatic fluids, wide hydrothermal systems, and their host rocks. In particular, massive amounts of CO₂ are released by calderas during unrest phases and have been often detected before eruptions. An accurate assessment of CO₂ sources is thus fundamental to properly understand gas monitoring signals during volcanic crises. We focused on the restless Campi Flegrei caldera, in southern Italy, where CO₂ fluxes at the Solfatara-Pisciarelli hydrothermal site have been progressively increasing up to 4000–5000 t/d during the ongoing unrest that started in 2005. Theoretical models of magma degassing have been able to reproduce the CO₂-N₂-He variations at the Solfatara fumaroles. However, a time-dependent deviation between measured and modeled N₂/CO₂ and He/CO₂, well correlated with the temporal evolution of ground uplift and temperature of the hydrothermal system, has been observed since 2005. We show that these variations are controlled by intense physical-chemical perturbation of the hydrothermal system, which is driving the decarbonation of hydrothermal calcite stored in reservoir rocks. This process is providing large volumes of non-magmatic CO₂ during the current unrest, contributing up to 20%–40% of the total fumarolic CO₂.

INTRODUCTION

Large amounts of CO₂ are transferred from deep inside Earth to the surface by volcanoes and their associated magmatic systems (Aiuppa et al., 2019; Fischer et al., 2019; Werner et al., 2019; Fischer and Aiuppa, 2020), as CO₂ is the second most abundant volatile species in magmas after water and becomes preferentially enriched in the exsolved magmatic gas due to its low solubility (Edmonds and Wallace, 2017). However, other sources of non-magmatic CO₂ can also occur, particularly at active calderas, where an intense interaction among magmatic fluids, wide hydrothermal systems, and their host rocks can take place. Discriminating the sources of CO₂ at volcanoes is fundamental because magmatic CO₂ can increase greatly before eruptions (Fischer and Chiodini, 2015).

In this study, we focused on the restless Campi Flegrei caldera (CFc, southern Italy;

Fig. 1), which has been characterized in the past 40 k.y. mainly by explosive activity ranging from large-scale ignimbrite (De Vivo et al., 2001; Pappalardo et al., 2008; Pappalardo and Mastrolorenzo, 2010, 2012; Albert et al., 2019) to minor Strombolian eruptions (Pappalardo and Buono, 2021). The last event occurred in 1538, after ~3000 yr of quiescence, and it was preceded by intense and long-term precursory phenomena (e.g., Di Vito et al., 2016; Liedl et al., 2019). After a period of subsidence following the last eruption, the caldera was affected by bradyseismic crises in 1950–1952, 1970–1972, and 1982–1984, and a new phase of unrest has been ongoing since 2005 (Chiodini et al., 2015a, 2021).

At CFc, deeply derived CO₂ is emitted at the Solfatara-Pisciarelli hydrothermal site both by soil diffuse degassing and by vigorous fumaroles (Fig. 1; Cardellini et al., 2017; Tamburello et al., 2019). The CO₂ fluxes increased in recent years up to 4000–5000 t/d (Chiodini et al., 2021), a value that ranks Campi Flegrei among the top

eight volcanic CO₂ emitters on Earth (Fischer et al., 2019; Werner et al., 2019). In addition to the dominant magmatic CO₂ emission (Caliro et al., 2007), a large amount of CO₂ is stored in the hydrothermal calcites included in the volcanic products of the shallow Campi Flegrei caldera-filling rocks (Chiodini et al., 2015b) and in the carbonates that are inferred to be present in the deep basement of the volcano (Zollo et al., 2008; Vanorio and Kanitpanyacharoen, 2015).

The emission of hydrothermal-volcanic gas at the Solfatara-Pisciarelli hydrothermal site has been systematically monitored over the past 20–40 yr (Caliro et al., 2007; Chiodini et al., 2021). We investigated the variations observed within the CO₂-N₂-He gas system; i.e., low or unreactive gas species among those routinely analyzed at CFc fumaroles. These gas species have been previously used to investigate magma dynamics at CFc and constrain long time series of geochemical data measured at Solfatara vents with thermodynamic modeling. Different proposed magma degassing scenarios accurately reproduce the measured CO₂-N₂-He trends at least from 1982–1989 (Caliro et al., 2014; Chiodini et al., 2015a, 2016; Buono et al., 2022). However, a systematic, time-dependent, and increasing deviation with respect to these theoretical models for N₂/CO₂ and He/CO₂ ratios can be observed from 2005 to today (Fig. 2).

This deviation, plausibly driven by the addition of non-magmatic CO₂, has remained uninvestigated until now. Interestingly, its time evolution appears to be very well correlated with the trend of the temperature in the CFc hydrothermal system, independently estimated by gas geoindicators, as well as with that of ground deformation signals (Figs. 3 and 4).

A comprehensive view of the processes involving the shallow (2–3 km) hydrothermal system at CFc during the ongoing unrest has

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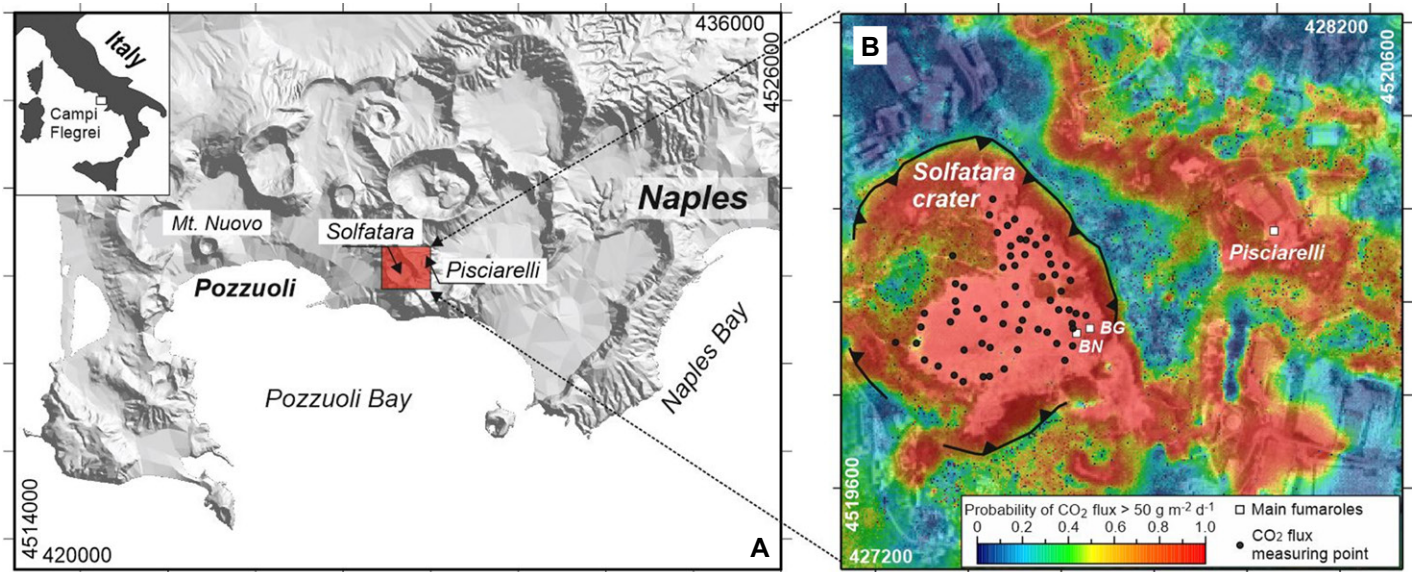


Figure 1. (A) Location map of the Campi Flegrei caldera in southern Italy. (B) Map of diffuse degassing structure at the Solfatara-Pisciarelli hydrothermal site (after Cardellini et al., 2003). Coordinates are expressed in UTM-WGS84.

been recently published. Particularly, a long-term process of heating in the system, driven by steam contributions and steam condensation, has been identified as the source of the accelerating ground deformation (Chiodini et al., 2015a), and the resulting increase in the pressure-temperature (P - T) conditions is thought to cause energy transfer from the fluids to the host rocks, triggering the microseismicity located at the base of the Solfatara-Pisciarelli system (Chiodini et al., 2021, and references therein). Consequently, it will be valuable to investigate if the hydrothermal calcite abundantly stored in the host rocks of the CFc hydrothermal system (Chiodini et al., 2015b) can produce additional CO_2 when exposed to the current abrupt physical and chemical perturbations.

N_2/He VERSUS N_2/CO_2 AND He/CO_2 RATIOS: ANALYTICAL DATA VERSUS MODEL RESULTS

Magma Degassing Models

In recent years, several studies have investigated geochemical changes within the CO_2 - N_2 - He gas system to explore deep magma dynamics at CFc. They combined geochemical data collected at Solfatara fumaroles with numerical simulations of different magma degassing scenarios, employing open-system magma degassing models for H_2O - CO_2 - N_2 -noble gas mixtures (for details, see Caliro et al., 2014; Buono et al., 2022).

A first effort was proposed by Caliro et al. (2014), who inferred that degassing of ascending mafic magma and/or mixing between mag-

matic fluids exsolved at various levels during magma ascent can properly reproduce the measured trends. More recently, two main scenarios were defined and proposed to explain fumarole compositions, constrained with additional monitoring signals:

(1) Continuous decompression-induced magma degassing (simple decompression scenario; Figs. 2A and 2B), consistent with fumarolic data since 1989, which is possibly driving the current unrest at CFc. The authors (Chiodini et al., 2015a, 2016) defined an initial pressure of 200 MPa (i.e., ~ 8 km depth assuming lithostatic control) but highlighted that variations in starting depth do not significantly affect the inferred degassing trends, which are mainly dependent on relative gas solubilities.

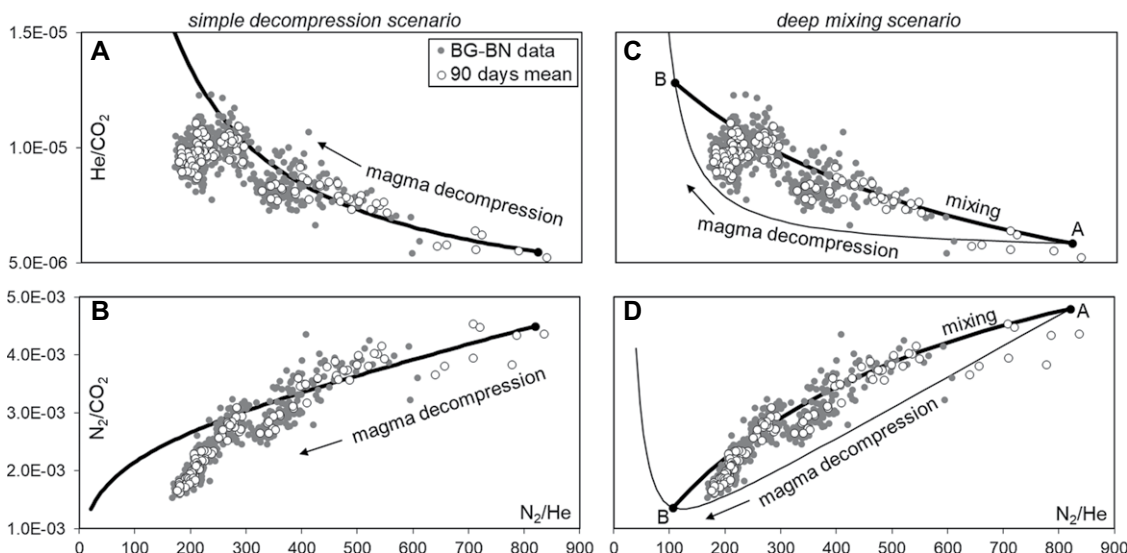


Figure 2. He/CO_2 (A,C) and N_2/CO_2 (B,D) versus N_2/He diagrams showing measured (and 90 d mean) versus modeled data for simple decompression (A,B) and deep mixing (C,D) degassing scenarios.

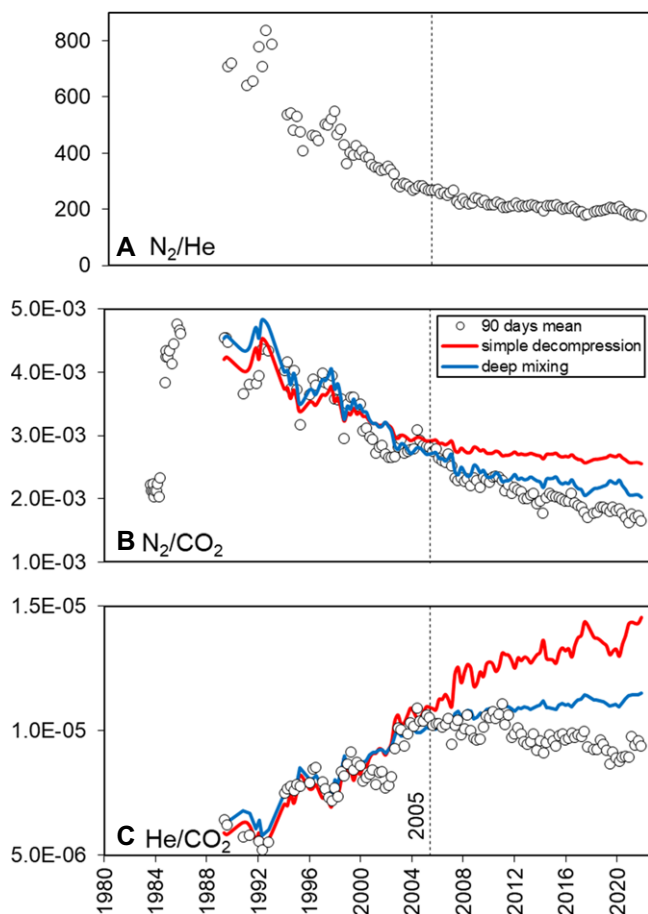


Figure 3. Chronograms of N_2/He (A), N_2/CO_2 (B), and He/CO_2 (C) measured and modeled (bold lines) ratios.

(2) Mixing of gases exsolved by magmas degassed at different depths along a decompression plus crystallization ascending path (deep mixing scenario; Figs. 2C and 2D). The authors (Buono et al., 2022), integrating detailed petrologic data to accurately constrain initial magmatic conditions (P - T , mol% CO_2), reconstructed a more composite scenario, where gases released by deep (400–300 MPa) magma accumulated at the base of the overlying hydrothermal system, driving the intense 1982–1984 crisis. The subsequent exhaustion and depressurization of the deep-signature gas reservoir caused the subsequent slow subsidence and seismic quiet, interrupted since 2005 by the ongoing unrest, which is possibly fed by intensifying degassing of the shallower magma reservoir (200 MPa) and the associated migration of fluids toward the hydrothermal system.

However, both the proposed end-member scenarios are able to fit measured data at the Solfatara vents. Therefore, we will consider both scenarios in order to investigate the origin of the additional CO_2 flux regardless of the assumed model for magma dynamics.

Comparison Between Observed and Modeled N_2 -He- CO_2 Compositions

The main Solfatara fumaroles (BG and BN in Fig. 1) have been systematically sampled

since 1983, and He has been routinely measured since 1989. The sampling rate of the fumaroles has varied in time from a few samples per year before 2000 to a monthly sampling frequency of the two fumaroles since 2000, when a geochemical laboratory devoted to the surveillance of Campanian volcanoes was installed at the Istituto Nazionale di Geofisica e Vulcanologia–Osservatorio Vesuviano (for details, see Caliro et al., 2007; Chiodini et al., 2021). In order to have a more homogeneous data set, we refer to the mean composition every 90 d for the two fumaroles (Table S1 in the Supplemental Material¹).

As already described, the measured compositions in the gas system N_2 -He- CO_2 are well reproduced by the results of magma degassing models (Fig. 2). Here, we refer to (1) a simple decompression scenario that reproduces the evolution of the gas composition of a decompressing mafic magma from 200 to 120 MPa (Figs. 2A and 2B); and (2) a deep mixing scenario that reproduces the variation in the gas

¹Supplemental Material. Details on mechanisms for hydrothermal calcite consumption (Figure S1) and Solfatara fumarole composition (Table S1). Please visit <https://doi.org/10.1130/GEOL.S.21992519> to access the supplemental material and contact editing@geosociety.org with any questions.

composition of a deep component released at 400 MPa (point A in Figs. 2C and 2D) by a trachybasaltic melt mixing with the gas emitted at lower pressure (210 MPa; point B in Figs. 2C and 2D) by the same type of magma after crystallization started.

The results of both scenarios are compared with the measured compositions in the N_2/He versus N_2/CO_2 and N_2/He versus He/CO_2 diagrams (Fig. 2).

Even though the measured compositions fit the theoretical lines well, there are some time-dependent deviations highlighted in the N_2/He , N_2/CO_2 , and He/CO_2 chronograms (Fig. 3). A well-delineated decreasing trend characterizes the N_2/He ratio from 1989 to the present (Fig. 3A). The N_2/CO_2 ratio shows a sharp increase from 1983 to 1985 and then a subsequent decrease (Fig. 3B). The He/CO_2 ratio shows an increase from 1989 to 2005 and a decrease after 2005 (Fig. 3C). We assume here that the regular decreasing trend in the N_2/He ratio since 1989 reflects the inert behavior of the two species; i.e., their content is fixed by the deep processes without modification during the ascent of the gas to the surface. Starting from the modeled curves of Figure 2, we found theoretical relationships (fourth-order polynomial regressions; $R^2 = 0.99$) between modeled N_2/CO_2 and He/CO_2 (dependent variables) and modeled N_2/He (independent variable) ratios; we then used the measured N_2/He ratio to compute the theoretical values expected for N_2/CO_2 and He/CO_2 ratios over time ($N_2/CO_{2,model}$ and $He/CO_{2,model}$; red and blue lines in Figs. 3B and 3C for simple decompression and deep mixing scenarios, respectively). Before 2005, measured He/CO_2 and N_2/CO_2 ratios fit the theoretical values reasonably well, while subsequent measured values progressively departed from the theoretical values. This systematic deviation can be explained by the progressive addition of CO_2 from a different source than the magmatic CO_2 .

We computed the amount of CO_2 to be added or subtracted to each mole of fumarolic fluid ($CO_{2,add}$ in moles/mole) so that measured He/CO_2 ratios equal the modeled ratios ($CO_{2,add} = CO_{2,measured} - He/[He/CO_{2,model}]$). Note that the same values of $CO_{2,add}$ were obtained using N_2/CO_2 instead of He/CO_2 .

In Figure 4, the $CO_{2,add}$ values are compared with two independent parameters:

(1) The maximum vertical displacement measured at Campi Flegrei, chosen to be representative of the time evolution of the volcanic unrest at Campi Flegrei in the past 40 yr (red line in Figs. 4A and 4C).

(2) The temperature of the hydrothermal system inferred by gas geothermometers, based on the CO/CO_2 ratio, applied to the Solfatara fumaroles (Fig. 4). These temperatures refer to the upper part of the hydrothermal system (~0.5 km

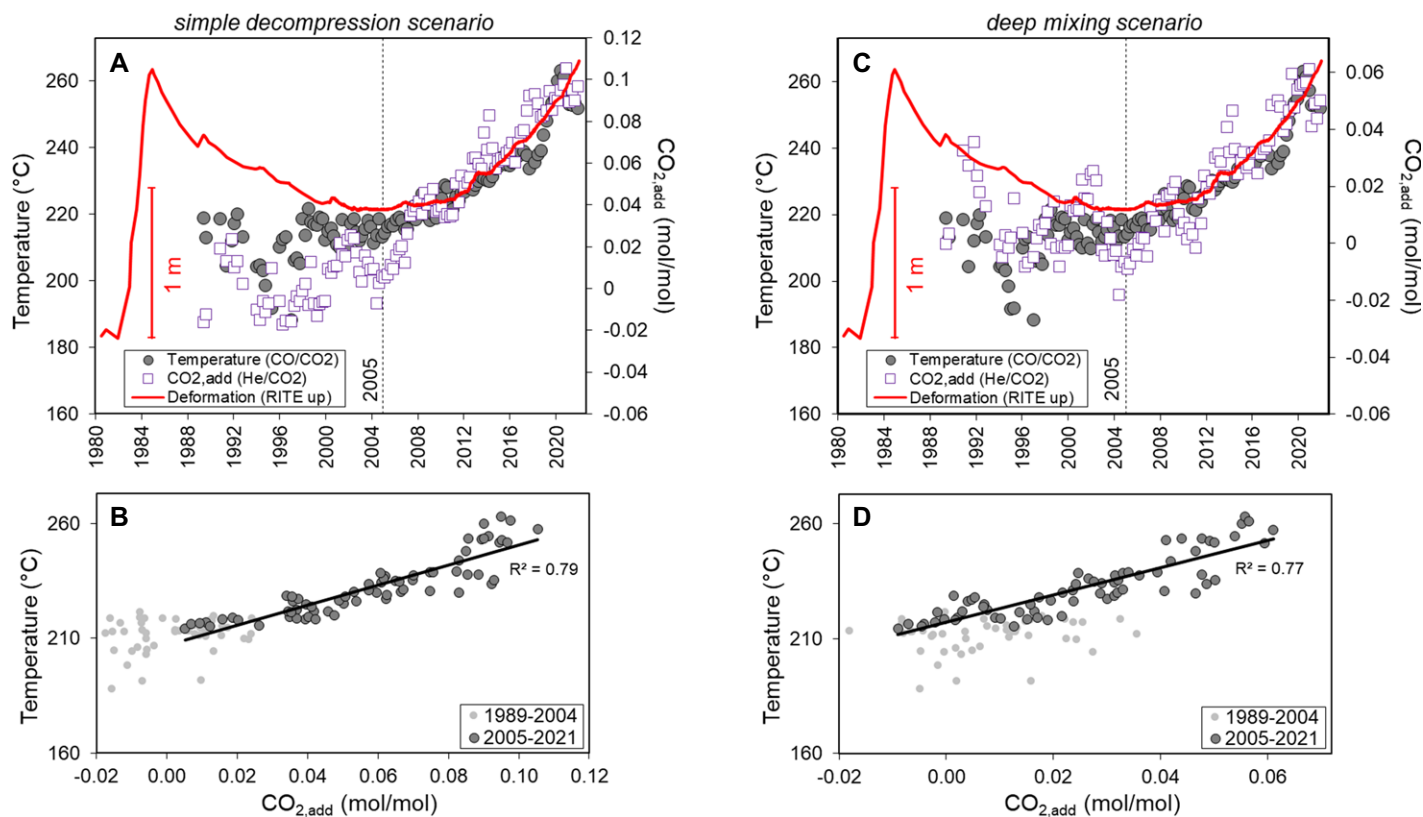


Figure 4. (A,C) Time variation of hydrothermal CO₂ (CO_{2,add}) compared with maximum vertical deformation (red line) and hydrothermal temperature, and (B,D) correlation between CO_{2,add} and hydrothermal temperature for simple decompression (A,B) and deep mixing (C,D) degassing scenarios.

depth; for details on the applied gas geothermometer, see Chiodini et al. [2021]).

As already discussed in previous studies, the post-2005 inflation phase of the caldera has been accompanied by a marked temperature increase in the hydrothermal system (Chiodini et al., 2015a). During the ongoing unrest (since 2005), CO_{2,add} has increased over time in a way similar to the temperature, a variable with which it is well correlated (Figs. 4B and 4D). It is worth noting that the correlation between CO_{2,add} and hydrothermal temperature is independent from the magma degassing model chosen as the reference scenario (Figs. 2 and 4). In summary, the comparison between measured and modeled compositions suggests that an external source of CO₂ became active at CFc in the middle of the 2000s concurrent with heating of the system. This external source of CO₂ is possibly the decarbonation of calcite found in the reservoir rocks of the CFc hydrothermal system (Chiodini et al., 2015b). In total, we estimate that this non-magmatic source of CO₂ contributes up to ~40% and ~20% of the total fumarolic CO₂ in the simple decompression and deep mixing scenarios, respectively.

DISCUSSION AND CONCLUSIONS

Chiodini et al. (2021) inferred that a temperature increase is occurring at the top of a gas-

dominated zone identified below the Solfatara-Pisciarelli area (Fig. 1). This gas plume extends vertically from a depth of 0.3 km to >2 km, representing a main source of the current seismicity at CFc. Petrologic and isotopic data from core samples of geothermal wells drilled into the upper 3 km highlighted that CFc subsurface rocks host high contents of hydrothermal calcite that fix large amounts of the volcanic CO₂ (Chiodini et al., 2015b). The intense physical-chemical variations occurring at CFc during the ongoing unrest, and in particular the heating of the system, can thus widely affect hydrothermal calcite, leading to the observed additional CO₂ flux.

There are at least three different mechanisms that may currently favor the formation of CO₂ starting from the consumption of hydrothermal calcite:

(1) The occurrence of a decarbonation reaction such as the breakdown of calcite, in the presence of quartz, to form wollastonite (calcite + quartz = wollastonite + CO₂; Okrusch and Frimmel, 2020). This “metamorphic” reaction requires temperatures higher than those inferred by gas geoindicators for the top of the hydrothermal system (200–260 °C; Fig. S1). Similar reactions could, however, occur in the deeper portion of the system, where magmatic fluids enter the hydrothermal system at high temperatures.

(2) In the hydrothermal system, the CO₂ fugacity (f_{CO_2}) can be fixed by reactions involving calcite and silicate rocks. Giggenbach (1984, 1988) suggested, e.g., that in a fully equilibrated hydrothermal system, the f_{CO_2} would be controlled by the following reaction: Ca-Al-silicate + K-feldspar + CO₂ = calcite + K-mica, where the Ca-Al-silicate indicates a mineral formed in the hydrothermal environment (e.g., laumontite, epidote, or wairakite; full equilibrium assemblage). In this context, a temperature increase within the hydrothermal system, such as that observed since 2005 at CFc, would favor the formation of CO₂ (Fig. S1). However, similar full equilibrium reactions require relatively long times (Giggenbach, 1984, 1988), which are probably not compatible with the rapid dynamics of the ongoing CFc unrest and heating.

(3) The dissolution of calcite by acid solutions that can be formed during the growing arrival of deep steam and its condensation to increase hydrothermal temperature. The temperature increase since 2005 has been explained by an increase in the input of magmatic fluids entering the system (Chiodini et al., 2016). Some of these fluids would condense, forming an increasing amount of acid solutions at the base of the system that could dissolve the hydrothermal calcite, forming CO₂. It is worth

noting that a marked increase in steam condensation at shallow levels since 2005 was inferred from the interpretation of fumarolic gas compositions coupled with concurrent measurements of CO₂ emission at Solfatara (Chiodini et al., 2021).

We conclude that the time-dependent deviation between measured and modeled N₂/CO₂ and He/CO₂ ratios since 2005, well correlated with temporal trends of hydrothermal temperature and vertical deformation, is controlled by the involvement of an external source of non-magmatic CO₂. Its origin can be associated with the decarbonation of hydrothermal calcite stored in reservoir rocks, driven by intense physical (i.e., heating and pressurization) and chemical changes in the hydrothermal system. The same processes are currently promoting microseismicity and ground uplift at CFC (Chiodini et al., 2015a, 2021).

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