

### ***Reply to the General comments of the reviewer***

In the first sentence of the General comments [*Marini et al. attempt to integrate new gas geochemical data and existing information into a revised “conceptual model” of the Solfatara magmatic-hydrothermal system at Campi Flegrei*], there is something wrong, in that we did not produce any new gas geochemical data, whereas we used the Solfatara geochemical database, produced in forty years, first by Cioni and coworkers and second by Chiodini and coworkers, with the aim to monitor the temperatures and total fluid pressures in the three reservoirs which are present at different depths in the Campi Flegrei caldera. As part of our work, we also revised the *conceptual model “of the Solfatara magmatic-hydrothermal system”*, integrating relevant geological data, both collected at the surface and obtained by the deep geothermal wells drilled by Agip-ENEL in the late ‘70s early ‘80s, and pertinent geophysical data.

For what concerns the second sentence of the General comments [*I found the manuscript very difficult to review as a lot of important information, namely regarding the methods, the underlying assumptions, uncertainty assessment, known vs. inferred geology, as well as the exact lines of reasoning from data to interpretation are missing*], we recall that, as written in the paper, the methods are the gas-geothermometers and gas-geobarometers specifically derived and calibrated for the Solfatara fumaroles. These gas-geothermometers and gas-geobarometers as well as their underlying assumptions are thoroughly described and discussed in the book of Marini et al. (2022), to whom the interested reader is referred because it would be out of place to repeat all these matters in our manuscript. The uncertainty of gas-geothermometers and gas-geobarometers cannot be assessed because this is an impossible exercise for fumarolic fluids’ geo-indicators, such as those elaborated and/or used by Cioni et al. (1984, 1989), Taran (1986), Giggenbach (1987), Tedesco and Sabroux (1987), Chiodini and Cioni (1989), Cioni and Marini (1990), Chiodini and Marini (1998), Caliro et al. (2007), Chiodini et al. (2011, 2015, 2016, 2017, 2021), Fiebig et al. (2013), Moretti et al. (2017, 2018, 2020), Buono et al. (2023) and many others. There is no inferred geology in our work. Again, we considered only known geological data, both collected at the surface and obtained by deep geothermal boreholes, as well as known geophysical data to revise the “conceptual model” of the Solfatara magmatic-hydrothermal system. Let us skip, for the moment, the sentence *exact lines of reasoning from data to interpretation are missing*; we will return on this point below.

For what concerns the following sentence of the General comments [*This renders the work in its current form essentially irreproducible and very difficult to review because essentially almost every paragraph can be challenged*]. We do not see any problem to reproduce our results, namely the temperatures and total fluid pressures in the three reservoirs which are present at depth in the Campi Flegrei caldera, in that anyone can use our gas-geothermometers and gas-geobarometers to obtain equilibrium temperature and total fluid pressure values. Thus, we do not see the reason for such a strong statement and the reviewer's mostly non-constructive comments.

Let us now consider the following sentence of the General comments [*Even some (central) elements of the discussion seem to contradict each other; e.g., the concept of separate “reservoirs” as locations of equilibration of different gas*

*geothermometers is obsolete with the assumption of flow through a vertically connected structure*]. Let us try to explain how it is possible that distinct gases (i.e., H<sub>2</sub>S, CH<sub>4</sub>, and CO) equilibrate at different temperatures and total fluid pressures in three reservoirs different but connected to each other by a fault zone along which a continuous compressible fluid flow occurs. To this purpose, let us assume that the branches of the fault zone extending from the magma chamber to the surface and connecting the three reservoirs to each other are small-diameter pipelines, the shallow reservoir volume contributing to the fumarolic discharge is a medium-diameter pipeline, and the intermediate and deep reservoirs' volumes contributing to the fumarolic discharge are large-diameter pipelines. The continuity equation written in a simple way for a compressible fluid flow is:  $Q = \rho \cdot A \cdot v$ , where Q is the mass flow rate (M/T),  $\rho$  is the density of the compressible fluid (M/L<sup>3</sup>), A is the cross-sectional area (L<sup>2</sup>), and v is the velocity of the fluid (L/T). Even if  $\rho$  is a function of temperature and pressure, the continuity equation implies that the fluids will move very fast along the fault zone, very slowly in the deep reservoir (in which fluids resides long enough to permit hydrogen sulfide re-equilibration) and in the overlying intermediate reservoir (in which fluids resides long enough to allow methane re-equilibration), and not so fast but not so slowly in the shallow reservoir (in which fluids resides long enough to allow carbon monoxide re-equilibration).

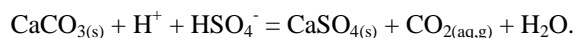
Let us now take into account the subsequent sentence of the General comments [*Also, regarding the core chemistry, the authors (apparently coming from a volcanology background) seem to rely on shallow fumarole gas equilibria and ignore established knowledge from the magmatic-hydrothermal systems community for the deeper and higher pressured parts of the system (e.g., H<sub>2</sub>S generation through the well-known SO<sub>2</sub> disproportionation reaction)*]. First of all, the reviewer's words "apparently coming from a volcanology background" are out of place, not to say offensive. The reviewer's words implicitly implies that she/he believes that volcanologists are second-class scientists, compared to the first-class scientists to which she/he belongs. What can we say? We are proud, all three of us, of our common background in geology. Concerning our specialization, two authors (LM and ML) are geochemists and the other author (CP) is volcanologist, unfortunately or fortunately for her. By the way, our scientific profile can be found at the following web pages:

<https://sites.google.com/view/luigimarini/home-page>      <https://scholar.google.it/citations?user=gBITrwsAAAJ&hl=it>  
<https://www.igg.cnr.it/organizzazione/personale-igg/matteo-lelli>

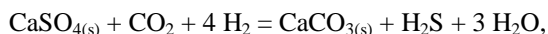
We do not rely on "*shallow fumarole gas equilibria*", because no gas species equilibrates at surface (fumarolic) conditions. Again, we used the chemistry of the Solfatara fumarolic fluids and the gas-geothermometers and gas-geobarometers of Marini et al. (2022), which were specifically derived and calibrated for the Solfatara fumarolic fluids, taking into account the deviations from the ideal gas behavior (an unprecedented exercise with respect to previous papers on gas-geothermometers and gas-geobarometers), to monitor the temperature and total fluid pressure, over a time interval of ~40 years: (i) in the shallow reservoir (0.25-0.45 km depth), where CO equilibrates; (ii) in the intermediate reservoir (2.7-4.0 km depth), where CH<sub>4</sub> attains equilibrium; (iii) in the deep reservoir (6.5-7.5 km depth), where H<sub>2</sub>S achieves equilibrium.

Moreover, the reviewer is wrong on our alleged ignorance on the *established knowledge from the magmatic-hydrothermal systems community for the deeper and higher pressured parts of the system*, because we are aware of the "*H<sub>2</sub>S generation*

through the well-known  $SO_2$  disproportionation reaction”, which is actually thoroughly discussed in Chapter 9 - The Redox Potential and Sulfur Gas Species of Marini et al. (2022) where it is numbered Eqn. (10). We take this opportunity to clarify that the  $SO_2$  disproportionation reaction produces not only  $H_2S$  (as written by the reviewer), which is a weak acid, especially at the high temperatures and pressures of interest, but also sulfuric acid, which is a strong monoprotic acid, as it is totally dissociated in bisulfate ion and hydrogen ion in the considered conditions. This means that the  $SO_2$  disproportionation reaction produces a strongly acidic aqueous solution. This aqueous solution reacts promptly with the carbonate rocks which are present above the Campi Flegrei magma chamber, according to the following reaction:



This is the same reaction explaining the widespread occurrence of anhydrite in the geothermal systems of Central Italy, such as Latera (Cavarretta et al. 1985; Marini and Chiodini 1994), even as part of the contact-metasomatism paragenesis, as well as in the geothermal system of Nisyros (Ambrosio et al. 2010), where again carbonate rocks and marbles are present above the magma chamber. The same reaction evidently occurs at the base of the deep reservoir which is present at depths of 6.5-7.5 km in the Campi Flegrei caldera. Anhydrite is the partner of calcite in the heterogeneous reaction:



representing the theoretical foundation of the  $H_2S$  gas-geothermometer and gas-geobarometer of Marini et al. (2022).

For what concerns the following sentence of the review [*I think that for these reasons the manuscript should not be published in its current form and requires a complete revise beyond “major revisions”*], we are willing to improve our manuscript in response to constructive and scientifically valid comments, but none of the previous ones meet these essential requirements.

We have no comment on the following sentence of the General comments [*In the following I will highlight some key problem areas (and for each one only some facets and ignore many questionable details) of the manuscript but will refrain from a detailed list of all issues*], which is the last one of the section General comments.

### ***Reply to the Specific comments 1: methods and assumptions behind them***

Let us consider the first sentences of the Specific comments 1 [*The authors rely on three gas equilibria to obtain “distinct equilibration temperatures and related total fluid pressures”. They do not elaborate how these were computed and not even how such a “equilibration temperature” is to be interpreted (e.g.: is it the lowest temperature at which the reaction went to equilibrium along the fluid’s upflow path and which was then preserved due to kinetic limitations at lower temperature?), and how such equilibrium could be demonstrated at all*]. In the sections Methods and Results of the revised manuscript, we added a few words to clarify these points. The gas equilibration temperature is the temperature at which the considered reaction or the considered key gas species (i.e.,  $H_2S$ ,  $CH_4$ , and  $CO$ ) attain chemical equilibrium. This is assumed to be

preserved at lower temperatures because reaction kinetics becomes too small. In general, in geothermometry and geobarometry, equilibrium cannot be demonstrated, it is assumed. Furthermore, in the case of Solfatara fumaroles, the computed equilibrium temperatures and pressures cannot be compared with any measured value, because the nearest deep geothermal well, called CF23/Agnano 1<sup>1</sup>, is found at a distance of ca. 1 km from the Solfatara fumaroles. This is a problem not only for our manuscript, but also for all previous geothermometric-geobarometric studies on the Solfatara fluids such as those of Cioni et al. (1984, 1989), Tedesco and Sabroux (1987), Chiodini and Cioni (1989), Cioni and Marini (1990), Chiodini and Marini (1998), Caliro et al. (2007), Chiodini et al. (2011, 2015, 2016, 2017, 2021), Fiebig et al. (2013), Moretti et al. (2017, 2018, 2020), Buono et al. (2023) as well as the monthly INGV Bulletins. We think that there is no need to recall the general considerations and assumptions which are common practice in geothermometric and geobarometric applications.

Let us now take into account the following sentences of the Specific comments 1 [*It remains completely opaque how the computations were done. I would argue that at least some of the stated computations are currently not meaningfully possible for the lack of adequate thermodynamic data and models, e.g. for a complex gas phase in equilibrium with a 21 or 33.5 wt% aqueous NaCl brine – for the conditions stated there exists neither an adequate solubility model for the gases in such a brine nor are even remotely accurate activity or fugacity coefficients available. How then could temperatures and pressures be derived? I tried to make my way through the main author’s 2022 book (375 pages, the main findings of which the present manuscript is supposed to summarize and explain) but I could not identify a coherent summary of the computations and the underlying assumptions with reasonable effort. This manuscript should deliver a crystal-clear and reproducible description and openly lay out and discuss the major assumptions to become a publishable contribution*]. Since gas species are assumed to equilibrate in a single saturated vapor phase in equilibrium with a 21 or 33.5 wt% aqueous NaCl brine, there is no need for an “adequate solubility model for the gases in such a brine”. Brine-vapor coexistence is assumed to fix H<sub>2</sub>O partial pressure. This is the only role played by the brine, in our approach, which is similar to that assumed by Giggenbach (1987). Fugacity coefficients of gas species were computed by Marini et al. (2022) following different approaches. First, the fugacity coefficients of H<sub>2</sub>O and CO<sub>2</sub> were obtained along the isenthalpic expansion path of Bocca Grande fluids of different composition: (i) by using the GERG-2008 thermodynamic module of the CONVAL Software Package and the virial EOS (see pages 102-111 of Marini et al. 2022), (ii) by using the Peng-Robinson EOS (see pages 111-118 of Marini et al. 2022), and (iii) from Table 3 in Appendix A of Gallagher et al. (1993) reporting the results of the EOS of these authors. Then, the three series of fugacity coefficients of H<sub>2</sub>O and CO<sub>2</sub> were compared (see pages 118-121 of Marini et al. 2022). After this comparison, Marini et al. (2022) decided to use the Peng-Robinson EOS to compute the fugacity coefficients of all the gas species of interest (not only H<sub>2</sub>O and CO<sub>2</sub>, but also H<sub>2</sub>S, H<sub>2</sub>, CH<sub>4</sub>, and CO) not only for the isenthalpic expansion path, but

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<sup>1</sup> Well CF23/Agnano 1 was drilled in the ‘50s by SAFEN “on the eastern slopes of the Solfatara relief and reached a total depth of 1841 m, where a maximum temperature of 325 °C was measured (Minucci 1964)”, as reported by Marini et al. (2022).

also for the linear P-T decompression path and the pressures and temperatures of coexistence of a brine containing 21 or 33.5 wt% NaCl with the related vapor phase (see pages 122-142 and pages 308-312 of Marini et al. 2022). Fugacity coefficients were then considered in the calibration of gas-geothermometers as discussed at pages 286-287, 335, and 344 of Marini et al. (2022). These explanations were synthetically added to the Introduction of the revised manuscript, to improve its clarity.

130 In the subsequent part of the Specific comments 1, the reviewer focuses again on the SO<sub>2</sub> disproportionation reaction [*There exists a relatively elaborate assessment of sulfur chemical behavior in the deep vs. shallow parts of magmatic-hydrothermal systems that was established some decades ago in the economic geology community (just to name the works by Einaudi and Hedenquist as an example) including the importance of “rock-buffered” vs. “direct degassing” paths. The very relevant insights presented there go largely ignored by the present authors. Namely, the important SO<sub>2</sub> disproportionation reaction to*  
135 *generate H<sub>2</sub>S (and there are variations of the theme depending on temperature, rock, etc.) is ignored although it is considered most important by many researchers in the field. The reactions (3) and (4) involving calcite also seem odd; most people working on the deeper parts of magmatic-hydrothermal systems would see these reactions going to the left (albeit possibly rather involving SO<sub>2</sub> and using plagioclase rather than calcite) to sequester sulfur rather than creating H<sub>2</sub>S, see, e.g., Henley et al., JVGR 2022. I wonder what “H<sub>2</sub>S temperatures” would come out if this was properly taken into account*  
140 *of if “H<sub>2</sub>S temperatures” would have any meaning then.*]

Above, we have already rejected this critique on the SO<sub>2</sub> disproportionation reaction. Since the reviewer refers to the works by Einaudi and Hedenquist, we take this opportunity to consider the paper by Einaudi, M. T., Hedenquist, J. W., & Inan, E. E. (2005). *Sulfidation state of fluids in active and extinct hydrothermal systems: Transitions from porphyry to epithermal environments*. [doi:<https://doi.org/10.5382/SP.10.15>], in which the authors contrast the oxidation and sulfidation states of  
145 fresh igneous rocks from arc environments and the sulfidation states of sulfide assemblages in calc-alkalic porphyry copper, porphyry-related base metal veins, and epithermal gold-silver deposits with compositions of fluids from active systems by plotting vapor compositions in  $\log f_{S_2} - 1,000/T$ ,  $R_H - 1,000/T$ , and  $R_S - 1,000/T$  diagrams, where  $R_H = \log (f_{H_2} / f_{H_2O}) \approx \log (X_{H_2}/X_{H_2O})$ ,  $R_S = \log (f_{H_2} / f_{H_2S}) \approx \log (X_{H_2}/X_{H_2S})$ , and X = mole fraction of the gas. It must be underscored that H<sub>2</sub> and H<sub>2</sub>S are apolar gas molecules, whose fugacity coefficients increase with increasing temperature and pressure, whereas H<sub>2</sub>O is a  
150 polar gas molecule, whose fugacity coefficient decreases with increasing temperature and pressure, as shown by Marini et al. (2022). Although the findings of Marini et al. (2022) refer, strictly speaking, to the Solfatara fluids, the fugacity coefficients of H<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>O are expected to vary in the same way, irrespective of chemical and physical conditions of the considered system, because in any case H<sub>2</sub> and H<sub>2</sub>S are apolar molecules and H<sub>2</sub>O is a polar molecule. Therefore, the assumption  $\log (f_{H_2} / f_{H_2S}) \approx \log (X_{H_2}/X_{H_2S})$  might still be correct to some extent, whereas the assumption  $\log (f_{H_2} / f_{H_2O}) \approx \log$   
155  $(X_{H_2}/X_{H_2O})$ , which was first proposed by Giggenbach (1987), becomes increasingly wrong with increasing temperature and pressure. We believe that works affected by these gross blunders do not represent the top of knowledge and those who present them in this way have a poor knowledge of gas geochemistry in magmatic-hydrothermal system. We do not

understand the reason to obstacle, in a non-constructive way, new works aimed at increasing the knowledge of new geo-indicators.

160 Since the “*reactions (3) and (4) involving calcite also seem odd*” to the reviewer, we underscore once again that in the Campi Flegrei, above the magma chamber, there is a thick sequence of carbonate rocks, as revealed by a number of geophysical studies on the active seismic reflection data of the SERAPIS survey and the passive seismic data of the 1982-1984 bradyseismic crisis (see references in our manuscript). The thick sequence of carbonate rocks occurring above the Campi Flegrei magma chamber is the same sequence cropping out all around the Campanian Plain, which has been  
165 downthrown by the boundary faults of the plain and other NW-trending tectonic structures (called Apenninic by Italian geologists) and has been dissected by the NE-trending conjugated structures (called anti-Apenninic by Italian geologists). The occurrence of these carbonate rocks above the magma chamber prompted us to use calcite (instead of plagioclase) as partner of anhydrite in reactions (3) and (4).

For what concerns the sentence of the Specific comments 1 “*most people working on the deeper parts of magmatic-hydrothermal systems would see these reactions going to the left (albeit possibly rather involving SO<sub>2</sub> and using plagioclase rather than calcite) to sequester sulfur rather than creating H<sub>2</sub>S, see, e.g., Henley at al., JVGR 2022*” let us comment separately on the use of “*plagioclase rather than calcite*” and on the direction of reactions (3) and (4).  
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We do not agree with the reviewer that “*most people working on the deeper parts of magmatic-hydrothermal systems*” would have used the “*plagioclase rather than calcite*”, because geologists know very well that geology is the first  
175 fundamental constraint that cannot be overlooked. We would certainly have considered reactions with plagioclase instead of calcite, if Al-silicate rocks were present above the magma chamber, but this is not the case at Campi Flegrei.

Reactions (3) and (4) are written here below for clarity:



180 For what concerns these two reactions, we would like to underscore that we do not care if they proceed from left to right (that is as they are written) or in the opposite direction, since, they are equilibrium reactions fixing H<sub>2</sub>S and CH<sub>4</sub> fugacities, respectively.

### ***Reply to the Specific comments 2: the core of the conceptual model***

185 Let us consider the first sentences of the Specific comments 2 [*When looking closer one has a hard time to understand reasoning behind the “conceptual model”. On the one hand, three “reservoirs” at different depth, separated by aquicludes, are postulated; on the other hand – to make the fluids migrate from a magma at >8km depth to the surface – connected flow through a vertically extensive “structure” needs to be invoked.*

190 *Now, first and foremost, I had a hard time understanding why the different gas equilibration temperatures should be specifically connected to the individual “reservoirs” and how the latter were inferred in the first place. Is there some circular reasoning? Or does actual, drilled geology with porosity and permeability measurements come into play? There is some mentioning of wells etc. but the exact reasoning remained blurry to me, at best. So, one cannot even tell if the depth of “reservoirs” and “aquicludes” is well-constrained or just a guess.]*

195 As already recalled above, the three reservoirs at different depth and the interposed aquicludes are not postulated, as written by the reviewer, but are constrained by known geological data, both collected at the surface and obtained by deep geothermal boreholes, which were drilled at depths from 1.5 to 3 km approximately, as well as by known geophysical data which were processed and interpreted by a number of studies. All is all, these data provide a well-constrained conceptual model extending to ca. 8 km where the magma chamber is located. There is no circular reasoning in the integration of geological and geophysical data to reconstruct the conceptual model of the Solfatara magmatic-hydrothermal system at Campi Flegrei, 200 that we did following the best practices used in geothermal exploration and other applied geo-sciences. To help the reader, we added a conceptual model cross-section of the system of interest, showing the shallow, intermediate, and deep reservoirs (Figure 5 of the revised manuscript).

205 Porosity and permeability measurements were performed on cores obtained in the deep geothermal boreholes, but obviously they do not extend at depths > 3 km approximately. These data are summarized by Rosi and Sbrana (1987). Nevertheless, they are not essential for the elaboration of the conceptual model, they would be much more important, not to say essential for the implementation of a numerical model, but this exercise is not among our aims.

210 The vertically permeable tectonic structure extending from the magma chamber to the surface and permitting the upward fluid flow through the three reservoirs and the interposed aquicludes “was activated during the final phase of the 1982-1984 seismic crisis along tectonic trends already active in the past (Rosi and Sbrana, 1987), as suggested by the occurrence of low-magnitudo earthquakes at depths of 0-8 km (D’Auria et al., 2011)” (see lines 320-323 of our manuscript). We take this opportunity to recall that large changes in several chemical components (e.g., N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S) of fumarolic gases occurred in the time interval May-September 1984 (e.g., Cioni et al. 1989; Caliro et al. 2014; Buono et al. 2022). They fit perfectly with the activation of this faulted-fractured zone and the transition from closed state to open state of the Solfatara magmatic-hydrothermal system, as discussed at lines 197 to 210 of our manuscript.

215 Although we have already explained above “*why the different gas equilibration temperatures should be specifically connected to the individual “reservoirs”*”, let us return again on this point to answer the reviewer. Accepting that there is a continuous, upward fluid flow along the vertically permeable tectonic structure extending from the magma chamber to the surface and, consequently, through the three reservoirs and the interposed aquicludes, the residence time of the fluids in each reservoir and in each aquiclude is expected to be directly proportional to the volume contributing to the fumarolic discharge 220 of each reservoir and each aquiclude; thus, the fluids will spend: (1) a relatively long time in the deep and in the intermediate

reservoirs because of their large volumes, even the fraction contributing to the fumarolic discharge; (2) a not too long and not too short time in the shallow reservoir because it has a volume much smaller than the deep and the intermediate reservoirs; and (3) a short or very short time in the aquicludes, where the volume available to fluid flow is small or very small. Moreover, in a given time interval, the temperature and total fluid pressure are expected to be constant or nearly so in  
225 the three reservoirs, whereas the temperature and total fluid pressure are expected to experience large upward decreases along the faulted-fractured zone crossing the aquicludes (see below for further details). Thus, in each one of the three reservoirs and in a given time interval, gas species are expected to attain equilibrium at a given temperature, total fluid pressure condition because of both the large or relatively large residence time and the constant or relatively constant temperature and total fluid pressure. In contrast, equilibrium temperature is expected to experience small re-adjustments  
230 during the transit from one reservoir to the other because of the small residence time in the aquicludes, in spite of the large decrease in temperature and fluid pressure.

Previous considerations clarify also the following sentences of the Specific comments 2 [*Then, if there is a vertically connecting structure – what is the meaning of the temperatures then? “Equilibration” will happen (and be “frozen in” if my above speculation about the meaning of “equilibration temperature” is correct) somewhere along the flow path and why  
235 should that be connected to the depth of any of the “reservoirs” then?*], whereas the following sentences of the Specific comments 2 call for some considerations [*Wouldn’t it make more sense that the increase in apparent temperatures and pressures (if correct) reflects rather a change in the hydraulic regime (or the degassing rate) such that the chemical signal of deeper fluids gets better preserved rather than a specific “reservoir” getting hotter and stronger pressurized (see, e.g., the overpressure waves in a magmatic-hydrothermal systems self-developing in the simulations of Weis et al., 2012; later  
240 suggested also by Lupi et al. for Campi Flegrei). What would speak for and against such different possibilities, why aren’t they considered and also tested against the data?*] Weis et al. (2012) implemented a numerical model to explain porphyry-type ore deposits, which is not relevant for the Solfatara magmatic-hydrothermal system at Campi Flegrei because the geological contexts are totally different. In fact, the three porphyry-style deposits considered by Weis et al. (2012), namely, Yerington in Nevada, Bingham Canyon in Utah and Batu Hijau in Indonesia are sustained by an unspecified source pluton or  
245 an unspecified inferred source pluton, whereas the Campi Flegrei volcanic area is characterized by a nested caldera with a magma chamber, whose top is positioned at ca. 8 km depth, probably hosting a trachyandesitic magma, according to Caliro et al. (2014) and Buono et al. (2022). It is unclear to us if the numerical model implemented by Weis et al. (2012) is able to reproduce the geological complexities of (at least) one of the three porphyry-style deposits because this crucial point is not discussed. Even more important, it is unclear to us the relation between the study of Weis et al. (2012) and our work, also  
250 considering that (1) the two time-windows are totally different (the time-scale of ore formation is between 50,000 and 100,000 years, whereas at the Solfatara we are considering a time interval of 38 years only), (2) we focus on the geochemistry of Solfatara fluids, whereas no data on fluid chemistry are given by Weis et al. (2012), apart from generic



sentences such as “We assume that, on cooling through the solidus temperature of 700°C, 5 wt% of the magma are released as aqueous fluid with 10 wt% NaCl through a cupola in the roof of the magma chamber.”

255 Lupi and coworkers speculate on the possible effects of large regional earthquakes on the Campi Flegrei magma chamber simulating “the propagation of elastic waves and show that passing body waves impose high dynamic strains at the roof of the magmatic reservoir of the Campi Flegrei at about 7 km depth. This may promote a short-lived embrittlement of the magma reservoir’s carapace, which is otherwise impermeable during inter-seismic times. Such failure allows magma and exsolved volatiles to be released from the magmatic reservoir. The fluids, namely exsolved volatiles and/or melts, ascent  
260 through a nominally plastic zone above the magmatic reservoir.” Although the idea might be interesting, the supporting evidence is not convincing at all. Again, the numerical model implemented by Lupi and coworkers is very generic and does not reproduce the geological reality of the Solfatara magmatic-hydrothermal system at Campi Flegrei.

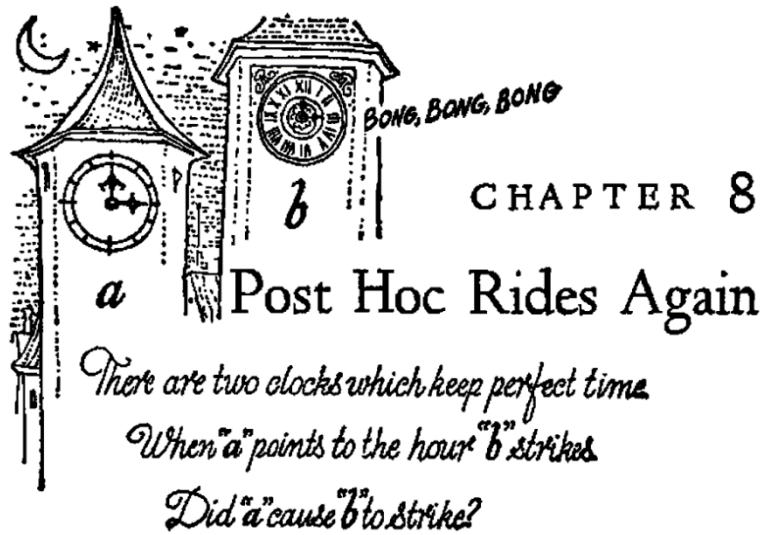
Even more important, the cause-effect relationship between regional earthquakes and uplift leaves much to desire. In particular, we wonder why the numerous regional earthquakes that occurred before 1945 (the beginning of the time window  
265 considered by Lupi and coworkers) did not activate any uplift at Campi Flegrei, which begun in 1950, according to Del Gaudio et al. (2010), or in 1945, according to the pioneering investigation of Ranieri (1952). In our opinion, the analysis of the cause-effect relationship between regional earthquakes and uplift is a good example of sample with the built-in bias, similar to the cases discussed by Darrell Huff in his masterpiece “How to Lie with Statistics”. Here below we report three examples taken from the book written by Darrell Huff:

270 (i) “Does early discovery of cancer save lives? Probably. But of the figures commonly used to prove it the best that can be said is that they don’t. These, the records of the Connecticut Tumor Registry, go back to 1935 and appear to show a substantial increase in the five-year survival rate from that year till 1941. Actually those records were begun in 1941, and everything earlier was obtained by tracing back. Many patients had left Connecticut, and whether they had lived or died could not be learned. According to the medical reporter Leonard Engel, the built-in bias thus created is ‘enough to account  
275 for nearly the whole of the claimed improvement in survival rate’.”

(ii) “A psychiatrist reported once that practically everybody is neurotic. Aside from the fact that such use destroys any meaning in the word “neurotic,” take a look at the man’s sample. That is, whom has the psychiatrist been observing? It turns out that he has reached this edifying conclusion from studying his patients, who are a long, long way from being a sample of the population. If a man were normal our psychiatrist would never meet him.”

280 (iii) “For further evidence go back to 1936 and the *Literary Digest’s* famed fiasco. The ten million telephone and *Digest* subscribers who assured the editors of the doomed magazine that it would be Landon 370, Roosevelt 161 came from the list that had accurately predicted the 1932 election. How could there be bias in a list already so tested? There was a bias, of course, as college theses and other post mortems found: People who could afford telephones and magazine subscriptions in

1936 were not a cross section of voters. Economically they were a special kind of people, a sample biased because it was loaded with what turned out to be Republican voters. The sample elected Landon, but the voters thought otherwise.”



In addition to the built-in bias in the sample considered by Lupi and coworkers, their cause-effect relationship between regional earthquakes and uplift might also be caused by chance, a common problem which is thoroughly discussed in chapter 8 of the book by Darrell Huff “Post Hoc Rides Again”.

290 Finally, for what concerns the last question of the Specific comments 2 [*What would speak for and against such different possibilities, why aren't they considered and also tested against the data?*] we underscore that it applies also to the works of Weiss and coworkers and Lupi and coworkers.

All in all, we have chosen to ignore the works of Weiss and coworkers and Lupi and coworkers to avoid criticizing them harshly in our manuscript. After all, every author should be allowed to publish her/his results, provided that they have scientific validity and are not affected by errors of any kind. We only want to underline that it is strange, very strange that the reviewers of the works of Weiss and coworkers and Lupi and coworkers have not noticed the problems discussed above that are so evident to our eyes.

300 Considering the following sentences of the Specific comments 2, [*In the whole conceptual model discussion, speculative ideas (such as Fournier's "self-sealing" quartz layer for which later studies found little evidence), inferred vs. drilled geology, geochemical data with different possible interpretations etc. are just mingled without testing for plausibility etc. Personally, I think that this is quite far away from best practices; the different ideas should be formulated as hypotheses and then tested to the degree possible*] first of all, it is funny to note that the masterwork paper written by Fournier (1999) is quoted without any criticism by Weiss and coworkers and Lupi and coworkers, but here the reviewer considers a speculative

idea the Fournier's "self-sealing" quartz layer for which later studies found little evidence. As written in the book of Marini et al. (2022), the reduction in permeability close to an intrusive heat source caused by quartz precipitation was discussed not only by Fournier (1999) but also in several other studies (e.g., Fournier 1985; Wells and Ghiorso 1991; Lowell et al. 1993; Moore et al. 1994; White and Mroczek 1998; Saishu et al. 2014; Scott and Driesner 2018), which possibly are unknown to the reviewer. Concerning the "best practices" to be followed in data interpretation, we agree with the reviewer and, as a matter of fact, we applied these "best practices" also in our manuscript, for example at lines 151-167, where we recalled different hypotheses to explain the gravimetric low present in the Campi Flegrei caldera, as well as, as another example, in the book of Marini et al. (2022) where, in chapters 6, 7, and 8, we took into consideration the different geothermometric-geobarometric approaches applicable to the H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>-CO-H<sub>2</sub> system. Afterwards, in the manuscript we selected a series of CO-, CH<sub>4</sub>- and H<sub>2</sub>S equilibrium temperatures and total fluid pressures (see lines 86-92 of our manuscript) to simplify the discussion and without pretending that these selected values are the indisputable truth. Nevertheless, if a different series of CO-, CH<sub>4</sub>- and H<sub>2</sub>S equilibrium temperatures and total fluid pressures is selected, the trend of increasing temperature and total fluid pressure with time is still observed although with some differences. Thus, there is little doubt, on the progressive pressurization of both the deep aquifer and the intermediate aquifer, as well as on the good correspondence between the chronogram of the intermediate aquifer overpressure and the chronogram of ground uplift (see lines 362-387 of our manuscript). Nevertheless, we are aware of the Karl Popper' words "whenever a theory appears to you as the only possible one, take this as a sign that you have neither understood the theory nor the problem which it was intended to solve" or, in simpler words ... we are so close to perfection that it scares us.

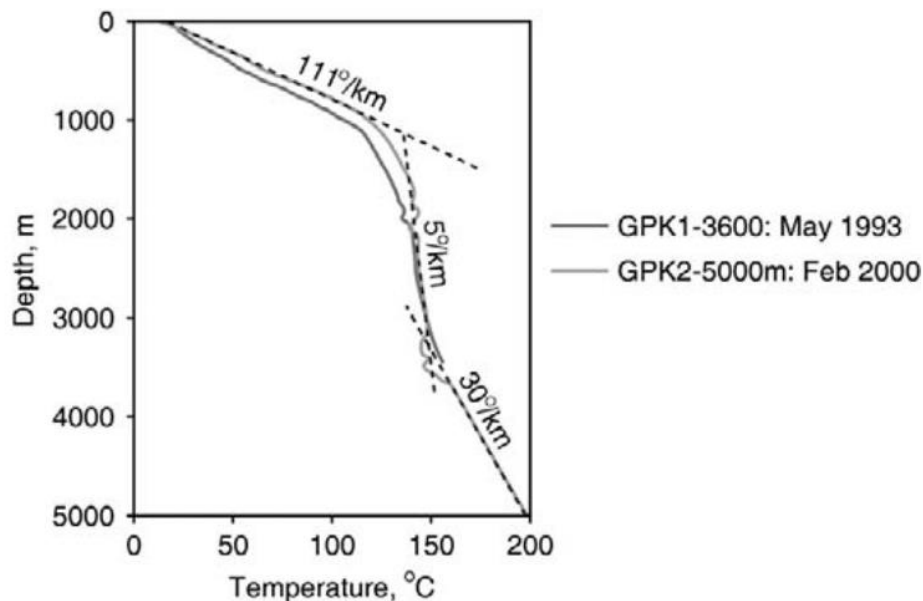
### ***Reply to the Specific comments 3: drawing straight lines without reasoning***

For what concerns the first sentence of the Specific comments 3 [*The temperature and pressure profiles in Figs. 5 and 6 hinge on the – untested – assumption that the gas equilibration temperatures are representative for three "reservoirs" at different depth*], we underscore that at lines 186-277 of our manuscript we have provided several pieces of evidence indicating that the three gas equilibration temperatures and related total fluid pressures refer to the three "reservoirs" positioned at different depths. We have proven that our geothermometers and geobarometers are effective tools to understand the processes controlling the bradyseism and to monitor the evolution of the bradyseismic crisis, as indicated by the correspondence, which is not coincidental, between the time changes in the overpressure of the intermediate reservoir and the time changes in ground movements. This is an important step forward compared to the CO-CO<sub>2</sub> equilibrium temperatures and pressures reported and discussed in all recent articles by Chiodini and coworkers, including the monthly INGV Bulletins. In fact, the CO-CO<sub>2</sub> pressure refers to the shallow hydrothermal aquifer and is too low to explain ground movements.

335 Our manuscript is not an academic exercise because to understand the processes controlling the bradyseism and to monitor  
the evolution of the bradyseismic crisis are crucial aspects for the scientific community and the Italian authorities in charge  
of the volcanic surveillance of Campi Flegrei to mitigate the natural risks in this densely populated area. To clarify this point,  
we added a few sentences in the section Conclusions.

Let us take into consideration the following sentences of the Specific comments 3 [In Fig. 5, temperature in each reservoir is  
340 taken to be constant. Unless I missed something important no reason is given why this should be the case. Rather, it is taken  
as granted (out of nothing) and then it is postulated that convection inside the reservoir homogenizes the temperature.  
Between the reservoirs – again: unless I overlooked something important – straight lines are drawn without reasoning and  
then it is stated that the “the heat transfer appears to be controlled by conduction”. I think this is quite poor scientific  
practice to just draw a straight line in the absence of data and then to assume it is correct and make such a conclusion.]

345 To answer these reviewer criticisms, we have reported below some relevant sentences, in blue color, from the textbook  
written by Malcolm A. Grant and Paul F. Bixley (2011) **Geothermal Reservoir Engineering**, Second Edition, which is “the  
only training tool and professional reference dedicated to advising both new and experienced geothermal reservoir  
engineers”. “The simplest distinction made in temperature profiles is between conductive and convective profiles. When  
rock is impermeable, heat is transported by conduction. This produces a characteristic profile where temperature increases  
350 linearly with depth; the gradient will change if there is a change in thermal conductivity of the rock.



**FIGURE 4.2** Temperature profiles in GPK-1 and GPK-2. Source: *Genter et al., 2009*. © Geothermal Resources Council.

Convection by contrast is a far more efficient means of heat transport than conduction. Once there is some permeability in the rock - and the required permeability is much less than what is needed for economic well performance - the fluid motion

355 controls the temperature distribution. Convective profiles can take a considerable variety of forms, with isothermal sections,  
inversions, boiling sections, and mixtures of all of these. Figure 4.2 shows temperature profiles from two wells at the  
engineered geothermal systems (EGS) project at Soultz, France (Genter et al., 2009). There are three sections on the profile.  
The first kilometer has a high gradient and linear profile, indicating conductive transport. Then from 1 km to 3.3 km there is  
360 is again a high linear gradient, indicating conductive heat transport and consequently lower permeability in the surrounding  
formations.

#### 4.4.2. Isothermal

An isothermal profile is a section of the well where the temperature is constant or nearly constant with depth. This can reflect  
circulation of fluid in a section of the wellbore or interzonal flow (without boiling), or it may be that the reservoir itself has  
365 isothermal temperatures due to convection.”

For what concerns the following sentences of the Specific comments 3 [*For fluid pressure (Fig. 6) the “reservoirs” are also  
drawn to have constant pressure even if more than a km high. This is obviously unphysical as there would have to be a  
hydrostatic pressure gradient (not necessarily linear as density of the fluid may vary with depth)*], the constant pressure over  
thicknesses of more than a kilometer is not unphysical as erroneously claimed by the reviewer. Instead, the vapor-static  
370 pressure or steam-static pressure gradient is a typical characteristic of vapor-dominated (dry-steam) systems, as discussed:  
(1) long ago by White et al. (1971) and Truesdell and White (1973), (2) in several later papers (e.g., Ingebritsen and Sorey  
1988; Williamson 1990; Scott 2020), in the textbook of Grant and Bixley (2011, see above) and (3) summarized in the book  
by Marini et al. (2022) at pages 190-191.

*Ingebritsen, S. E., & Sorey, M. L. (1988). Vapor- dominated zones within hydrothermal systems: Evolution and natural  
375 state. Journal of Geophysical Research: Solid Earth, 93(B11), 13635-13655.*

*Scott, S. W. (2020). Decompression boiling and natural steam cap formation in high-enthalpy geothermal systems. Journal  
of Volcanology and Geothermal Research, 395, 106765.*

*Williamson, K. H. (1990). Reservoir simulation of The Geysers geothermal field. In Proceedings of the Fifteenth Workshop  
on Geothermal Reservoir Engineering, Stanford University, Stanford, California, January 23-25, 1990 SGP-TR-13.*

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#### **Some other specific comments**

*I only list a few, which I think are important:*

- *1: I think that a Google Earth snapshot is a no-go and contains much less info than, e.g., a simplified line art map  
385 showing the main geologic structures and the main geographic locations. Add a square that show the location of  
Fig 1b. In 1b show a scale rather than an unexplained coordinate system.*

- Avoid self-celebrating statements in the introduction.
- “standard deviation” in line 98 includes what? Just the effect of variable gas analysis? What’s the uncertainty of the thermodynamic analysis to obtain T and P? Possibly much larger?
- I can’t follow the reasoning in 4.3; if you assume that (1) and (2) work well separately, than (5) should work as well as it is simply a linear combination of the two, right?

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Please find our answers here below:

(i) As already recalled above, we are geologists and geologists like Google Earth maps because they are very informative. For example, the senior author of our manuscript (LM) is co-author of the book by Cioni R., Marini L. 2020. A Thermodynamic Approach to Water Geothermometry, Springer Geochemistry Series, 415 pp, containing several Google Earth maps. In Figure 1a we added a square showing the location of Figure 1b. Since kilometric coordinates are reported on the two axes of Figure 1b, there is no need to show a scale in Figure 1b, because it would be redundant. We added this explanation to the caption of Figure 1b.

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(ii) We assume that the self-celebrating statements, which are not specified by the reviewer, are the words in red in the section from line 66 to line 69, which is reported here “Recently, we proposed new gas geothermometers and geobarometers, which were suitably calibrated for different plausible expansion paths of the Solfatara fluids, also considering the deviations from the ideal gas behaviour, **for the first time**. Our results were presented and thoroughly discussed by Marini et al. (2022). In this work, we summarize the main findings of Marini et al. (2022), taking into account the last data produced by Buono et al. (2023) for Bocca Grande and Bocca Nuova fumaroles for October 2020 to January 2022. Moreover, in this work, we use our geothermometric and geobarometric results, as well as the information from other disciplines (e.g., surface geovolcanological surveys, data from geothermal deep wells, and geophysical investigations) to elaborate a revised conceptual model of the Solfatara magmatic-hydrothermal system which extends at magmatic depths (~8 km) and **represents a considerable step forward with respect to previous conceptual models**.” If so, there is nothing wrong and no self-celebration in our words and we do not see any reason to omit these sentences simply reporting the truth.

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(iii) The standard deviation given in Tables A1 and A2 is just the standard deviation of the CO-, CH<sub>4</sub>-, and H<sub>2</sub>S-equilibrium temperatures and related total fluid pressures of each time interval (incidentally, these standard deviations can be verified using the values reported in the supplementary material). In other words, the standard deviation given in Tables A1 and A2 is “just the effect of variable gas analysis”. The uncertainty of computed equilibrium temperatures and related total fluid pressures includes several contributions, such as the uncertainties on the third law entropy and on the enthalpy of formation from the elements which are reported in the following table (from Chase, M. 1998. NIST-JANAF Thermochemical Tables, 4th Edition. Journal of Physical and Chemical Reference Data, Monograph No. 9, 1951 pp. <https://srd.nist.gov/JPCRD/jpcrdM9.pdf>)

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Gas species	Error on $\Delta H_f^\circ$	Error on $S^\circ$	Upper T
	kJ/mol	J/(mol K)	K
CH <sub>4</sub>	0.34	0.04	6000

CO	0.17	0.04	6000
CO <sub>2</sub>	0.05	0.12	6000
H <sub>2</sub>	0	0.033	6000
H <sub>2</sub> O <sub>(L)</sub>	0.042	0.079	500
H <sub>2</sub> O <sub>(V)</sub>	0.042	0.042	6000
H <sub>2</sub> S	0.8	n.r.	6000
SO <sub>2</sub>	0.21	0.08	6000

The uncertainty of computed equilibrium temperatures and related total fluid pressures also includes the uncertainties on the Maier-Kelley coefficients (which are small for gas species because their  $C_p$  values are well constrained), on the fugacity  
420 coefficients (on the fourth or third decimal figure), as well as the uncertainties related to the regression analysis performed to obtain the different geothermometric and geobarometric equations. Nevertheless, the major effect is probably the variability of analytical data.

(iv) In case of overall (full) equilibrium, the CO-equilibrium temperature related to reaction (1), the CH<sub>4</sub>-equilibrium temperature related to reaction (2) and the CO-CH<sub>4</sub>-equilibrium temperature related to reaction (5) are the same, with  
425 deviations from a few degrees to a few dozen degrees. For the Solfatara fluids, this overall equilibrium was observed until 1985. Afterwards, the CO-equilibrium temperature related to reaction (1) remained nearly constant, the CH<sub>4</sub>-equilibrium temperature related to reaction (2) increased more and more with time, and the CO-CH<sub>4</sub>-equilibrium temperature related to reaction (5) increased but much less than the CH<sub>4</sub>-equilibrium temperature. The ensuing increasing difference between the three temperatures is due to CO-CH<sub>4</sub> disequilibrium. In this case, the CO-equilibrium temperature and the CH<sub>4</sub>-equilibrium  
430 temperature are still meaningful, whereas the CO-CH<sub>4</sub>-equilibrium temperature is meaningless. Further details are given by Marini et al. (2022) at pages 209-215, where the CO-equilibrium temperature is called T(RWG), the CH<sub>4</sub>-equilibrium temperature is called T(SS4) and the CO-CH<sub>4</sub>-equilibrium temperature is called T(CCC). We decided to stop to use the SS1, SS3 and SS4 acronyms and other acronyms used by Marini et al. (2022) because we were told that they were reminiscent of Nazi SS.

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