

Public justification (visible to the public if the article is accepted and published):

Dear authors

In the following you will find my judgment on your revised version.

Marini and collaborators apply new geoindicators they have recently developed on the basis of a set of homogeneous and heterogeneous equilibria for the thermo-barometric interpretation of la Solfatara fluids (Campi Flegrei). The authors propose, after integration with independent geological and geophysical datasets, a new conceptual model for the Solfatara magmatic-hydrothermal system. The new conceptual model proposes that Solfatara fluids equilibrate at three distinct depths and T-P ranges, connected to the surface by a network of fractures. Their model stresses the role of the deepest reservoirs with the ongoing bradyseism. The paper concludes on the possible scenarios that can be deduced when embracing this new conceptual frame.

The research approach is rich, based on an extensive knowledge of the volcanic systems and specifically of the Campi Flegrei. The topic is obviously relevant and of major interest at local and global scale.

The review process was the opportunity of an in-depth exchange between the authors and the reviewers. As sometimes occur, major scientific debates are intertwined with passionate expression of each legitimate position. The role of the Editor is, besides appreciating the intense exchange in animating an important scientific debate, to propose a summary and to identify all possible constructive contributions that make science progress.

Here, I attempt to take some distance from the fiery debate (and I want to thank both the reviewers and the authors for providing abundant food for that) and I try to summarize a set of key points which I consider need to be carefully considered by the authors in order to further progress in the review process. My main advice is that the authors have extensively answered most of the remarks and criticism expressed by the reviewers, but that some key information has not been integrated yet in this last version of the manuscript.

My suggestion is to produce a new version enriched by the many elements shared or stressed online during the review process and relevant to help the reader to understand each step which has led the authors to their important conclusions. This new version must take into account all key points identified by the review process, summarized below.

Authors' reply: We agree with the Editor and we have amended the manuscript following his appreciated indications. We preferred to limit the changes to the main text to a minimum, in order to maintain the common thread that we believe will facilitate the reading of our article. However, we added distinct appendices both to provide the key information that was missing in the first version of our manuscript and to answer the remarks and criticisms of the reviewers, sometimes harsh, but still appreciated because they have allowed us to improve the quality of our paper. Here below, we provide a point-by-point reply to the comments of the Editor.

#Methods

Both reviewers have stressed the importance of integrating a detailed discussion of the assumptions and limitations of the adopted method in a specific paragraph. Currently, some information is missing in the manuscript, other is disseminated between the Introduction and the

Methods paragraph. The paper builds on a book where the reader can find more detailed information. Nevertheless, the manuscript (and associated appendix and supplementary file) must provide all relevant information. That is mandatory in order to guide the readers, most important those having less experience in the modelling and interpretation of fluid geochemical datasets, along the whole path leading to the new conceptual model.

Many important points have been stressed in the review process and they have to be integrated in the manuscript (e.g. the assumptions underlying the new gas-geothermometers and gas-geobarometers and most important their P-T-X range of validity; the influence of the tested T-P saturation decompression paths on the calculated P-T values; the possible influence of correction for the presence of CO₂ and halides in the vapor phase; the influence of the choice of the %NaCl brine for the calculations and the properties of homogeneous supercritical fluids. Most of these topics have actually been addressed in the set of replies provided by the reviewers. I suggest they are integrated both in the manuscript and in a specific Appendix emphasizing the assumptions and limits of the adopted approach.

Assumptions have been well explained in the review process and now they need to be made fully explicit in the manuscript.

Authors' reply: all the assumptions and limitations of gas-geothermometers are reported in Appendix C, apart from the assumption on the equilibrium coexistence of an almost pure saturated vapor phase with a very small amount of brine, which is found in the main text at lines 134-144. In Appendix C, assumptions and limitations are discussed in the following sections:

C.1. General assumptions

C.2. The saturation decompression paths: assumptions and limitations

C.3. The linear P-T decompression path: assumptions and limitations

C.4. The isenthalpic decompression path: assumptions and limitations

Among the assumptions, I would also mention, for instance, the choice of vapor-static vs hydrostatic pressure gradients, because considered typical of vapor-dominated dry steam systems.

Authors' reply: The increase in pressure from the top to the bottom of the intermediate and deep reservoirs was computed to a first approximation by using Eqn. (21), see lines 435-441. As mentioned at lines 476-479, due to the relatively high density of the fluids stored in both reservoirs, the pressure gradient turned out to be non-zero. This outcome is in contrast with the zero-pressure gradient typical of vapor-dominated geothermal systems (e.g., White et al., 1971; Truesdell and White, 1973; Grant and Bixley, 2011), where P, T conditions are similar to those of the shallow reservoir and significantly lower than those of the intermediate and deep reservoir.

Uncertainty assessment

The authors state (and that needs to be stressed in the manuscript) that absolute values of time series of T and P rely on selected/tested decompression paths, but that relative evolution is similar.

Basically, that implies that the conclusions of the manuscript do not rely on absolute values. More globally, the authors argue that uncertainty associated with the sampling+analytical procedure and fluid variability over a given time interval is larger than that related to the thermo-barometric calculations.

Authors' reply: In the main text, at lines 115 to 134, we clarified how the different expansion paths were considered in the calibration of the CO₂-, CH₄-, and H₂S-geothermometers and how many times series of equilibrium temperature and total fluid pressure were obtained for each geothermometer and geobarometer. These T, P time series are 4 for the CO₂-geoindicators (which gives similar results), 3 for the CH₄-geoindicators (which gives somewhat different results), and only 1 for the H₂S-geoindicators. This means that only the outcomes of the 3 CH₄-geoindicators have to be compared. We did this comparison in Appendix B, where we explained also why we chose the saturation (21 wt% NaCl) decompression path among the three time-series given by the CH₄-geoindicators.

However, the review process was the opportunity to discuss the applicability of the EOS (Peng-Robinson) chosen by the authors at temperatures >500°C and in occurrence of variable proportions of NaCl in the vapour phase together with the influence of CO₂ in the saturated vapour on the NaCl content of the liquid. When discussing the uncertainties, the role of the assumptions permitting to adopt the approximation of a CO₂ bearing vapor phase in equilibrium with a vapor-saturated H₂O-NaCl liquid and most important the possible role at high T of the mutual solubilities on the definition of saturation pressure must be included. Both the authors and the reviewer 1 agree on the upper limits (600°C and 1000°C for the 20% and 33% NaCl brines, respectively) of applicability of the equations. The most recent datasets approach or overpass these limits. Do the authors consider that their model can still be applied to the most recent datasets?

Similarly, a general agreement exists on the need of new experiments in the ternary H₂O-NaCl-CO₂ system. This can be discussed and linked to the assumptions made by the authors.

Authors' reply: These points are discussed in appendices A and C. In appendix A, we stressed the importance of considering the deviations from the ideal gas behavior in geothermometric calculations and we recalled the contrasting behavior, with increasing P and T, of the fugacity coefficient of H₂O and non-polar gases (CO₂, CH₄, CO, H₂S, and H₂) and the related implication on gas geothermometers. We also discussed the effects of mutual solubilities on fugacity coefficients and we explained why these effects were disregarded by Marini et al. (2022).

In Appendix C, as already recalled above, we discussed uncertainties, assumptions, limitations and applicability of the geoindicators calibrated for the different expansion paths. In particular, we focused on the two saturation paths, because they were finally adopted in our paper. Thus, we recalled the characteristics of the unary system H₂O, of the H₂O-CO₂ binary system, and of the H₂O-NaCl binary system, explaining why we adopted the last one to link P and T. We agree that it would have been much better to use the H₂O-NaCl-CO₂ ternary system, but this is not feasible at present, because of the lack of experimental data which complicates, not to say prevents, the derivation of

reliable EOS for the H₂O-NaCl-CO₂ ternary system. We agree that new experimental data for H₂O-NaCl-CO₂ ternary system are urgently needed.

Discussion section

Again, here the assumptions or available constraints concerning the time spent by the fluids in each reservoir and/or along the flow path, the extent and depth of the re-equilibration process etc need to be made explicit for the reader. The integration of geochemical and geophysical/geological datasets is at the core of the new conceptual model.

Authors' reply: As discussed in Appendix E, we tried to estimate the residence time spent by the fluids in each reservoir, taking our conceptual model as reference, assuming steady-state conditions, and specifying the total volume (rocks + fluids), the effective porosity, and the T, P conditions of each reservoir, as well as the flow of fluids through the system (from the CO₂ flow measured at the surface and the $X_{\text{H}_2\text{O}}/X_{\text{CO}_2}$ ratio of fumarolic fluids). Unfortunately, due to the poor knowledge of the effective porosity and its possible changes with time due to different factors (e.g., ground uplift, seismicity, mineral dissolution/precipitation), it is impossible to make reliable evaluations of the residence time of fluids, even for the shallow reservoir.

For instance, Reviewer 1 proposes alternative explanation to the modelled increase in T and P, arguing that this might result from a change in the hydraulic regime or degassing rate, allowing the deep chemical signal of fluids to be better preserved.

The discussion can also remind how much room is left for alternative explanations.

Authors' reply: This alternative explanation proposed by reviewer 1 was discussed by Marini et al. (2022) who noted that *“the increasing SS4 [CH₄] equilibrium temperature with time allows for two distinct implications, either (1) fumarolic fluids came from progressively deeper zones of the Solfatara magmatic-hydrothermal system, characterized by gradually higher fluid pressures and temperatures, or (2) fumarolic fluids came from the same deep permeable zone which experienced a progressive increase in fluid pressure and temperature with time.”* However, implication (2) explains the pressurization of the intermediate aquifer and the consequent ground uplift, on which there is a consensus in the scientific literature, whereas implication (1) does not. This is why we adopted the second implication in our paper. We added these considerations at lines 218-223.

Reviewer 1 suggests that calculated overpressures in the deepest reservoir are unrealistic and that ductile rocks cannot sustain that. This point needs to be addressed in the discussion section.

Authors' reply: This point was briefly recalled in the discussion section of the manuscript at lines 513-514 and was thoroughly discussed in Appendix F.

A link must thus be proposed in order to make explicit the influence of selected decompression paths on calculated pressures and the implications of estimated overpressures.

Authors' reply: This point is discussed in Appendix B. In particular, since the differences between distinct CH₄ equilibrium temperatures and pressures are <25°C and <200 bar in 2013-2021, the computed CH₄ equilibrium temperatures and pressures are almost independent of the considered

decompression path in the last years and the error in the estimated overpressure (Fig. 8a) is similar to or even less than short-term fluctuations.

Some important conclusions are stressed in the online replies, and can be better emphasized in the manuscript. For instance, the fact that CO-CO₂ equilibrium P-T form the current basis of monitoring activity and that they rely to the shallowest reservoir and that these pressures are considered too low to explain the ongoing bradyseism is an important conclusion and can be better emphasized.

Authors' reply: The fact that CO-CO₂ equilibrium P-T, forming the current basis of monitoring activity, refer to the shallow reservoir and that these pressures are too low to explain the ongoing bradyseism was recalled in the Conclusions.

In conclusion, the last (modified) version of the manuscript integrates only part of the answers provided to the reviewers and misses some key points (e.g. the important overpressure in the deepest reservoir; the applicability of the model for high T domains etc). If you agree to produce a new version integrating i) an appendix to summarize the main assumptions and limitations of the model and ii) the missing points in the discussion part, I will be glad to consider the manuscript for possible publication in SE.

Best regards

Massimo Coltorti

Authors' reply: We hope we answered all the requests by the Editor and that the manuscript is now suitable for publication in SE.

Best regards,

Matteo Lelli