

Reply to the second series of comments of reviewer n.1

PLEASE NOTE THAT THE REVIEWER'S WORDS ARE IN RED COLOR AND OUR REPLY IS IN BLACK COLOR.

Thank you for the reply, but I must admit that I feel that the contents of my previous review rather got confirmed than refuted. In the following, after a personal introductory remark, I will provide a second, in-depth review of several aspects of the study that will unambiguously demonstrate that key calculations are deficient with the consequence that key parts of the results on pressure lack scientific validity and that likely the temperatures as well are questionable. I will conclude with an incomplete list of answers to the authors rebuttal on points where I find that it may be beneficial for clarification.

Introductory remark

Let me start with a personal remark on the reviewing effort. A significant part of the authors' rebuttal is in essence "we explained this in the book Marini et al., 2022". And that was my very point in my previous commentary: a lot of information that is essential to allow a competent, science-focused review (or simply: a read) of the manuscript is not in there. It was submitted as a *research* article and as such should contain sufficient information about the concept, methods and assumptions to allow the reviewer an informed preparation of checking for, quoting the authors, "scientific validity and ... errors of any kind". I estimate that a few manuscript pages on Methods with carefully chosen and explained content would have guided the reviewer (or just reader) well enough to decide whether and what to follow up or not by reading the book or parts of it and they would have much increased the value of the manuscript. The manuscript condensed ca. 150 **pages** in the book to ca. 15 **lines** for the "Methods" and made not a single statement on important underlying concepts, assumptions, limitations, etc. This would have been even more important as the authors claim to have introduced novel tools.

In the version that I reviewed I was essentially forced to explore the book in quite some depth to just get the basics of what was performed in the study, not even to then follow up on the science done. I take peer reviewing serious and I am happy to spend two or three full working days for an in-depth review of an interesting manuscript (as I did then). But, here, this was not leading me anywhere close to understanding the full line of arguments, approaches, assumptions etc. for this study. The book does not make it easy for the reader to detect that information, which is often hidden in very long technical discussions that frequently get as detailed as instructing the reader about how to copy values around in Excel spread sheets (I am not criticizing that this is documented, it is great it is, but it just makes the book a very hard read). For me this was the first time in more than three decades of reviewing that I encountered a paper that expects reading a book in-depth before it can be understood. In essence, this meant reviewing the (published!) book, not the manuscript. I hope the authors may understand that this felt like them making my reviewer job as hard as possible and that I did not feel positive about the extra, in my opinion unnecessary, time effort.

In the "Introductory remarks" section the reviewer emphasizes that the review of our paper was very difficult and time-consuming and that "*he/she was essentially forced to explore the book in quite some depth to just get the basics of what was performed in the study*" and "*it was the first time in more than three decades of reviewing that*" the reviewer "*encountered a paper that expects reading a book in-depth before it can be understood*". This is a totally unfair and unjustified criticism since our work is self-consistent. We simply did not consider necessary to rewrite the equations of geothermometers and geobarometers in the main text because they are reported in the EXCEL spreadsheet, which is part of our paper as supplementary material. If one wants to understand how we derived these equations, she/he can read the book, but it is a personal choice which, we believe, should be motivated only by scientific interest and not by other reasons. For what concerns the sentence "... the authors claim to have introduced novel tools" we want to clarify that we do not claim to have done it, we simply did it. And this is not mendacious self-praise, but it is the pure and sacrosanct truth. For what concerns our book, let us say that it was already reviewed by competent scientists

before its publication. For what concerns the critiques of the reviewer of our book, let us say that they are unsolicited, because nobody asked the reviewer to review our book, they are a petty ploy to discredit both the book and our manuscript and they are written with ethically inappropriate words and style and denote a total lack of respect towards us.

Additional Review

Now, although my duty was to review the manuscript and not the book, I felt challenged by the style and content of parts of the rebuttal (some more words on that in the answer list in the third part of this reply) and dived rather deeply into some parts of the “thermometry” and “barometry”, which I already felt look suspicious when browsing the book before for understanding what was done in the study. After that new exercise (another two full working days including writing this reply), I make my recommendation even stronger:

The manuscript should be rejected because (at least) the pressure calculations for the middle and deep “reservoirs” (and likely the associated thermometry as well, at least for the deep and likely also for the middle “reservoir”) are based on a fundamentally invalid assumption and are, therefore, scientifically invalid in their current form. Even if the calculations were formally valid, the pressures would be based on an arbitrary, assumed (without constraints from data or theory) temperature-pressure path, i.e., again scientifically not constrained. As these invalid results form the very core of the study’s main contribution – the “revised conceptual model” and the important conclusions resulting from it – the manuscript cannot be accepted.

Notabene (after the experience how the previous review was perceived): I do acknowledge that a lot of honest effort and care were put into the underlying calculations in the book; nevertheless, I am convinced that a key problem escaped the authors’ attention, which, unfortunately, renders the “saturation decompression path” invalid, no matter how much effort was put into the calculation concept and its execution and no matter how exciting the results might look to the authors. That I use frank words should not be confused with disrespect but as a way to keep the discussion clear about the problem and keep it focused on the science; and not be shifted again to a scientifically meaningless competition on how experienced and qualified either reviewer or authors might be in different subareas of magmatic-hydrothermal systems research or in applying the respective community’s wording sufficiently accurately to be accepted (on that: I regret that the omission of “thermometry” in “new gas geochemical *thermometry* data” escaped my attention when proof-reading my review).

The first 25 lines of the Additional Review section [from “Now, although my duty...” to “... escaped my attention when proof-reading my review).”] are very verbose and do not concern the manuscript review. In fact, the reviewer shifts the focus from the manuscript (as it should be) to the book, looking for deficiencies in the book itself. From the unsolicited and unrespectful review of the book (see our previous comment), the reviewer seems to have realized that it is not possible to demonstrate that fluids follow the "saturation decompression path" on which geothermometers and geobarometers rely on and therefore the manuscript is not publishable. Regardless of the fact that the reviewer could have reached this conclusion based on the manuscript alone and that there was no need to read the book, we totally agree with the reviewer that it is impossible to demonstrate that the Solfatara fluids follow the saturation decompression path for a brine with a certain NaCl content rather than a different decompression path. Furthermore, we emphasize that the decompression path of the Solfatara fluids is totally unknown, as it is unknown for all fluids and all geothermometers, not only the gas geothermometers, but also the water geothermometers. Therefore, following the line of reasoning of the reviewer, one reaches the conclusion that all fluid geothermometers are based on wrong assumptions and all geothermometric results for all hydrothermal-magmatic systems

worldwide are wrong. Furthermore, since the databases of computer codes such as PHREEQC, EQ3/6, WATCH, SOLVEQ and others assume saturation conditions for pure water, also multicomponent geothermometry provides wrong results, again following the line of reasoning of the reviewer. In a nutshell, all the geochemical literature that deals with fluid geothermometry would be wrong and useless.

Alternatively, isn't it perhaps wrong to adopt the reviewer's point of view?

It is true that all geothermometers are based on hypotheses, including the decompression path during the ascent of the Solfatara fluids, but it is also true that in the book (not in the paper, for reasons of space) we have considered not only the saturation decompression paths but also other possible decompression paths, namely, the isenthalpic decompression path and the linear P-T decompression path. The CO₂, CH₄ and H₂S equilibrium temperatures and total fluid pressures (obtained considering the saturation decompression paths) were selected in the paper to simplify the discussion and without pretending that the selected values are the indisputable truth. Nevertheless, if a different series of CO₂, CH₄ and H₂S equilibrium temperatures and total fluid pressures (obtained considering a different decompression path) is selected, the time-trends of nearly constant CO₂-equilibrium temperature and total fluid pressure and increasing CH₄ and H₂S temperature and total fluid pressure are still observed with some limited differences. We will add these considerations to the revised manuscript.

Now to the core problem. The calculations of gas equilibration temperatures involve thermodynamics-based corrections for strong pressure effects. The pressures and resulting temperatures rely on an **arbitrary, assumed temperature-pressure path** along which fluids would have to flow on their way from the magmatic source to the fumaroles 8 km above where the samples were taken. The study tries to pinpoint where on that generic path individual parts of the actual Solfatara system are located.

According to the book, this assumed "saturation decompression path" is an arbitrary selection. It takes the vapor saturation pressure for a constant composition liquid (21 wt.%) in the pure H₂O-NaCl binary and adding a simplistic pressure correction for the presence of CO₂ in the vapor phase (as a side remark I wonder how one could call that "in equilibrium with a brine"; but see discussion of CO₂ solubility below). I like to emphasize again that this is an *assumed, arbitrary* path and not supported by any data; that "Giggenbach did that as well in 1987" is not a good geology- or physics-based justification. Pressures for the "reservoirs" are then "computed" by taking the computed gas equilibration temperatures and locating them on that path (I assume this was an iterative procedure).

Above we have anticipated our answers to the general introductory considerations of the reviewer and we have little to add here apart from two reviewer's sentences.

The first sentence is *'that "Giggenbach did that as well in 1987" is not a good geology- or physics-based justification'*. It is not our intention to point out that what we did is correct because Giggenbach had already done it in 1987. Our intention is to give Caesar what belongs to Caesar and to give Giggenbach what belongs to Giggenbach, who had the great merit to understand the complexities of natural systems and to develop geochemical tools easy for everyone to use. Werner Giggenbach was an unsurpassed master in this aspect.

The second sentence is *"Pressures for the "reservoirs" are then "computed" by taking the computed gas equilibration temperatures and locating them on that path (I assume this was an iterative procedure)."* There is no iterative procedure in our calculations. This is obvious to anyone who opens the EXCEL spreadsheet, which is part of our paper as supplementary material. We wonder if the reviewer has opened our EXCEL spreadsheet because we have serious doubts about it based on this sentence. If so, it would be a very serious negligence of the reviewer. But since we are not certain, we do not want to create a case without foundation.

In contrast, the key problems raised by the reviewers are undermined by several, sometimes specious, inaccuracies.

In a nutshell, the key problems of that approach are (more, illustrated detail then further below):

- A vapor-saturated 21 wt% NaCl brine that the calculations are based on simply doesn't exist above ca. 590 °C (the critical temperature for that composition in the binary H₂O-NaCl system¹ [footnote 1: btw., Giggenbach (1987) also stated that the validity is limited to ca. 600°C]), so the calculation is meaningless for all inferred temperatures for the deep "reservoir" and for the hottest of the middle one.

Here the reviewer reinvents the wheel. In fact, at pages 290-292 of the book we wrote that the RWG and SS4 geoindicators for the saturation decompression path of Solfatara fluids involving a brine containing 21 wt% NaCl and the related vapor phase can be used up to 600 °C. The maximum SS4 computed temperature, that is, the maximum CH₄-equilibrium temperature, 645°C, is not much higher. In our manuscript we wrote clearly that the CH₄-equilibrium temperature and total fluid pressure refer to the intermediate ("*middle*" in the reviewer's words) reservoir. We do not understand why the reviewer writes that "*the calculation is meaningless for all inferred temperatures for the deep "reservoir"*" because **the CH₄-equilibrium temperature does not apply to the deep reservoir**. This is an unacceptable reviewer's mistake.

- Instead, above that temperature, an H₂O-NaCl fluid on the two-phase liquid-vapor surface in that system is a vapor itself.
- As a major consequence, and as the critical line for 21wt% NaCl (with respect to water) in the ternary H₂O-NaCl-CO₂ system is nearly isothermal at those 590 °C: if CO₂ is present, the fluid at such high temperature and pressure conditions would be a homogeneous, "supercritical", dense vapor-1 btw., Giggenbach (1987) also stated that the validity is limited to ca. 600°C like fluid for which no unique P-T coordinates can be constrained without serious further assumptions.

It is interesting to note that the reviewer agrees with Giggenbach (1987) when it is convenient and vice versa. Well, we all agree on the maximum temperature at which the geoindicators for the saturation decompression path of Solfatara fluids involving a brine containing 21 wt% NaCl and the related vapor phase can be used, 600 °C.

- For this dense vapor-like fluid, due to the presence of significant NaCl and even if the pressures were correct, the fugacity coefficients calculated by the authors via a Peng-Robinson equation of state for a system without NaCl likely are in error (and, as far as I recall, standard P-R equations of state are not very well suited to include electrolytes) and so would be the gas thermometry.

This critique of the reviewer is totally wrong because there are many papers dealing with the use of the Peng-Robinson EOS, with some adjustments/modifications, to model vapor + liquid equilibria in electrolyte solutions and specifically in systems including water, sodium chloride, and carbon dioxide (e.g., Nighswander et al. 1989; Kwak and Anderson 1991; Søreide and Whitson 1992; Sieder and Maurer 2004; Baseri and Lotfollahi 2011; Hou et al. 2013; Appelo 2015; Li et al. 2015; Zuo et al. 2024). In particular, Appelo (2015) used the Peng–Robinson EOS to compute reliable fugacity coefficients for CO₂. He noted that the ion interaction parameters given by Harvie et al. (1984) for CO₂ at 25 °C are valid for calculating the CO₂ solubility at high temperatures, pressures and salinities.

Furthermore, use of the Peng-Robinson EOS is totally justified because we obtained comparable values, for the fugacity coefficients of CO₂ and H₂O, utilizing the GERG-2008 EOS (Kunz and Wagner 2012) and the EOS of Gallagher et al. (1993). To the best of our knowledge, fugacity coefficients were not considered in gas geoindicators proposed so far in the scientific literature, although use of fugacity coefficients is absolutely necessary at the high temperatures and pressures of CH₄ and H₂S equilibration. To be noted also that, irrespective of the decompression path, the fugacity coefficients of non-polar gases (i.e., CO₂, CO, CH₄, H₂, and H₂S) increase with increasing P, T, deviating gradually from unity, whereas the fugacity coefficient of H₂O decreases with increasing P, T, departing progressively from one. The ensuing practical implication is that the

analytical mole fraction ratios of non-polar gases (e.g., CO/CO₂, CH₄/CO₂, and H₂S/CO₂) may be utilized in geothermometric-geobarometric functions without incurring excessive errors, whereas use of the analytical H₂/H₂O mole fraction ratio leads to significant errors in computed equilibrium temperatures and pressures. **Summing up, the errors in fugacity coefficients and gas thermometry the reviewer refers to are totally non-existent while serious errors are committed if the fugacity coefficients are not considered.**

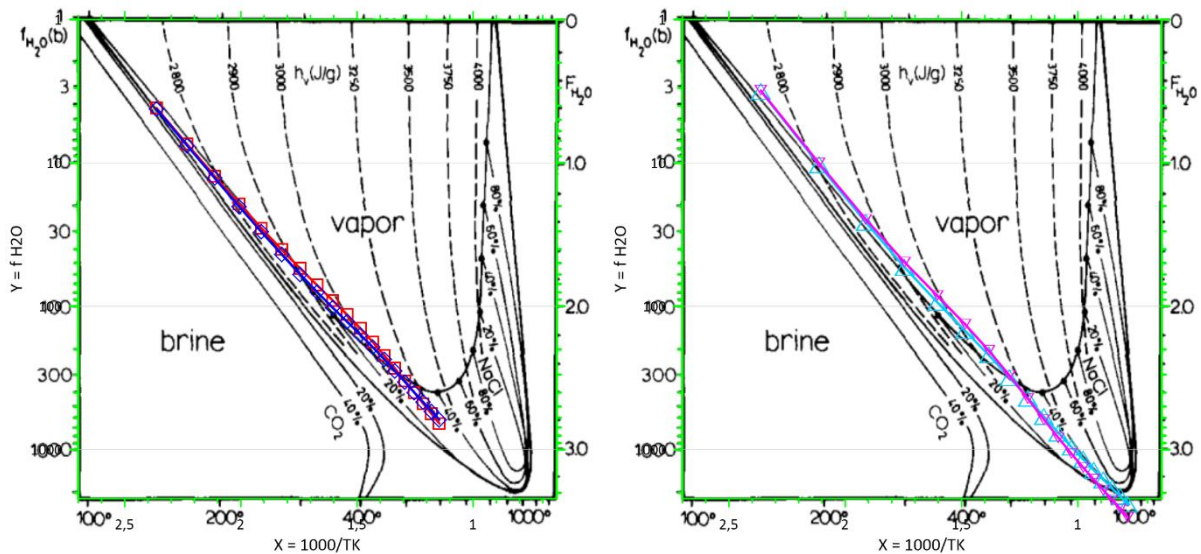
• These points render the temperature-pressure calculations for the deep “reservoir” in their present form invalid. How wrong they are in terms of numbers cannot be estimated in a simple way.

This critique of the reviewer is also not justified because (1) the T-P conditions of the deep reservoir are described by the H₂S equilibrium temperature and total fluid pressure and (2) the H₂S equilibrium temperature and total fluid pressure were computed considering the decompression path of Solfatara fluids involving a brine containing 33.5 wt% NaCl (not 21 wt% NaCl as erroneously considered by the reviewer) and the related vapor phase. Both things are written clearly in our manuscript. These functions can be used up a maximum pressure of 3627 bar and a maximum temperature of 1000 °C (see pages 335 of the book). In practice, the maximum H₂S equilibrium temperature and total fluid pressure computed for the Solfatara fluids, 1087°C and 3408 bar, are slightly higher and somewhat lower of these applicability thresholds, respectively. **So, there is nothing wrong in the temperature-pressure calculations for the deep reservoir as speciously claimed by the reviewer.**

• Moreover, the approximation of a carbonic vapor phase pressure in “equilibrium” with a vapor-saturated H₂O-NaCl liquid is only acceptable if the mutual solubilities of CO₂ in the aqueous solution and of water in the carbonic vapor phase are small such that the saturation condition spreads only over a small pressure interval and remains close to the saturation line in the aqueous solution binary.

These statements of the reviewer are unclear and contain some inaccuracies. The core or what we are talking about is if it is acceptable or not to refer to the saturation line of the aqueous solution binary H₂O-NaCl for a ternary H₂O-NaCl-CO₂. As shown in Figure 5 of Giggenbach (1987), this approximation is acceptable if the concentration of CO₂ in the brine and the concentration of NaCl in the vapor phase are both sufficiently low and not when the *mutual solubilities of CO₂ in the aqueous solution and of water in the carbonic vapor phase are small* as erroneously claimed by the reviewer (perhaps a typo?). On this figure, in the left-hand diagram, we have reported both the logarithm of the fugacity of water for a brine containing 21 wt.% NaCl in equilibrium with a vapor phase with a mole fraction of CO₂ equal to 0.05 (diamonds and line of blue color) and 0.40 (squares and line of red color), corresponding to the minimum and maximum mole fraction of CO₂ of interest for the Solfatara fluids. In the right-hand diagram, we have reported both the logarithm of the fugacity of water for a brine containing 33.5 wt.% NaCl in equilibrium with a vapor phase with a CO₂ molar fraction equal to 0.05 (upward pointing triangles and line of sky-blue color) and 0.40 (downward pointing triangles and line of magenta color). In both diagrams, the two lines with symbols are close to each other and their acceptably good linearity holds true up to 600°C for the brine containing 21 wt.% NaCl and up to 1000°C for the brine containing 33.5 wt.% NaCl. These lines are not positioned exactly between the vapor and brine envelopes reported in Figure 5 of Giggenbach (1987) because Giggenbach used the data of Sourirajan and Kennedy (1962) for the system H₂O-NaCl, whereas we used the data of Tanger and Pitzer (1989) for the brine containing 21 wt% NaCl and the data of Driesner and Heinrich (2007) for the brine containing 33.5 wt% NaCl. Moreover, Giggenbach took the fugacity coefficients, presumably of pure gases, from Ryzhenko and Volkov (1971) and Ryzhenko and Malinin (1971) and stated that “*for a separate gas phase containing water vapor as the major component, $x_{H_2O} > 0.8$, maximum pressures [not given] are controlled by the formation of an aqueous phase. Under these circumstances the isomolar ratios of activity coefficients $\gamma_{SO_2}/\gamma_{H_2S}, \gamma_{CO}/\gamma_{CO_2}, \gamma_{CO_2}/\gamma_{CH_4}, \gamma_{N_2} \cdot \gamma_{H_2O}/\gamma_{NH_3}^2$, and $\gamma_{H_2}/\gamma_{H_2O}$ [γ 's are actually fugacity coefficients] never deviate much from unity, and uncorrected mole-ratios may be used without incurring excessive errors*”.

In contrast, we computed the fugacity coefficients of gas species in gas mixtures using the Peng-Robinson EOS.



In spite of these minor deviations between our $f_{\text{H}_2\text{O}} - 1/T(\text{K})$ relations and the vapor and brine envelopes reported in Figure 5 of Giggenbach (1987), the clear description given by Giggenbach in his 1987 paper is still valid and is reported here: **“Three fluid stability regions can be distinguished: (1) a single liquid (brine) at comparatively low temperatures and high pressures; with increasing temperature or decreasing pressure a boundary (“liquidus”) is reached to a region (2) where a vapor phase will coexist with a saline brine; further increase in temperature, or reduction in pressure, will lead to complete evaporation of increasingly saline brines and to a boundary (“vaporus”) delineating the stability region (3) of a single vapor phase (in the presence of solid NaCl).”** In the Solfatara hydrothermal-magmatic system, the most probable condition is the coexistence of a vapor phase with a saline brine, because the occurrence of the other possible conditions is highly unlikely. In fact:

- On the one hand, the occurrence of a single liquid (brine) at comparatively low temperatures and high pressures is at variance with the huge amount of heat released from the magma batch and transferred to the overlying hydrothermal part of the system.
- On the other hand, a single vapor phase coexisting with solid NaCl might occur in depressurized vapor-cored magmatic systems (Reyes et al. 1993), such as Vulcano Island, Italy (Cioni and D’Amore 1984), and many systems of Indonesia (Abiyudo et al. 2016) and The Philippines (Reyes et al. 1993; Ramos-Candelaria et al. 1995; Apuada and Sigurjonsson 2008), but it is at variance with the current pressurization and related ground uplift of the Solfatara hydrothermal-magmatic system.

This holds true for typical geothermal systems at less than ca. 300ish °C and has, therefore, indeed be applied to such systems. As soon as the mutual solubilities are non-negligible (starting at $T > \text{ca. } 300\text{ish } ^\circ\text{C}$, some people might claim 350ish °C, it really doesn’t matter much) this is not possible anymore as “saturation pressure” of the liquid is not uniquely defined and phase compositions will change with phase proportions for a given bulk composition.

Rather, the liquid saturation pressure will now also be a function of the additional CO_2 content of liquid, i.e., there is a whole saturation surface over very wide ranges of pressure and for temperatures up to the near-isothermal (the above 590 °C) critical curve of the pseudo-binary “21 wt% aqueous NaCl solution + CO_2 ” instead of a single saturation line.

These theoretical considerations of the reviewer are correct but they do not apply to the Solfatara hydrothermal-magmatic system, in its current state, as discussed above. Things might have been different in the past and might be different in the future, as discussed in Chapter 11 of our book.

Side remark: so much about the authors' statement "there is no need for an "adequate solubility model for the gases in such a brine"."

We did not write this wrong sentence, neither in the paper nor in the book. At pages 122-123 of the book, we wrote that "... the binary H_2O -NaCl system is considered here, instead of the ternary H_2O -NaCl- CO_2 system, to describe brine-vapor coexistence both: (1) to avoid complicating the calculations too much and (2) because of the incomplete knowledge of the P-V-T-X properties of the H_2O -NaCl- CO_2 system, which is largely based on the experimental work by Gehrig (1980) and the P-V-T-X data obtained through the synthetic fluid inclusion technique (e.g., Kotelnikov and Kotelnikova 1990; Frantz et al. 1992; Johnson 1992; Shmulovich and Graham 1999; Schmidt and Bodnar 2000).

In addition to the determinations relevant for the binary H_2O - CO_2 system (see Sect. 2.1), Gehrig (1980) measured the molar volume and defined the immiscibility boundaries for the (H_2O +6 wt.% NaCl)- CO_2 pseudobinary system at pressures from 0 to 3000 bar and temperatures from 200 to 560 °C using a high-pressure variable volume autoclave. The data of Gehrig (1980) represent the main experimental foundations of the modified Redlich–Kwong EOS of Bowers and Helgeson (1983) as well as of the EOS of Duan et al. (1995), both for H_2O - CO_2 -NaCl fluids. Bowers and Helgeson (1983) computed fugacity coefficients of H_2O and CO_2 at temperatures of 400, 450, 500, 550, and 600 °C and pressures of 500, 1000, and 2000 bar and used these fugacity coefficients together with solubility data to establish the compositions of the coexisting immiscible phases. However, the EOS of Bowers and Helgeson (1983) was questioned by Duan et al. (1995). According to Duan et al. (1995), their EOS predicts P–V–T–X data, immiscibility/phase equilibria, solubilities, and activities with an accuracy similar to that of the experimental data at temperatures from 300 to ~1000 °C and pressures from 0 to 6000 bar for NaCl concentrations to ~30 wt% (relative to NaCl + H_2O) and to ~50 wt% with lower accuracy. However, the EOS of Duan et al. (1995) was considered poorly reliable by other authors (e.g., Schmidt and Bodnar 2000).

Given this situation, the binary H_2O -NaCl system was considered in this work, instead of the ternary H_2O -NaCl- CO_2 system, to describe the equilibrium coexistence of the vapor phase with a brine containing either 21 wt% NaCl (data from Tanger and Pitzer 1989) or 33.5 wt% NaCl (data from Driesner and Heinrich 2007)."

Our opinion on this topic is exactly the opposite of what the reviewer attributed speciously to us, in that, we believe that there is a need for an EOS able to predict P-V-T-X data, immiscibility/phase equilibria, solubilities, and activities in the ternary H_2O -NaCl- CO_2 system.

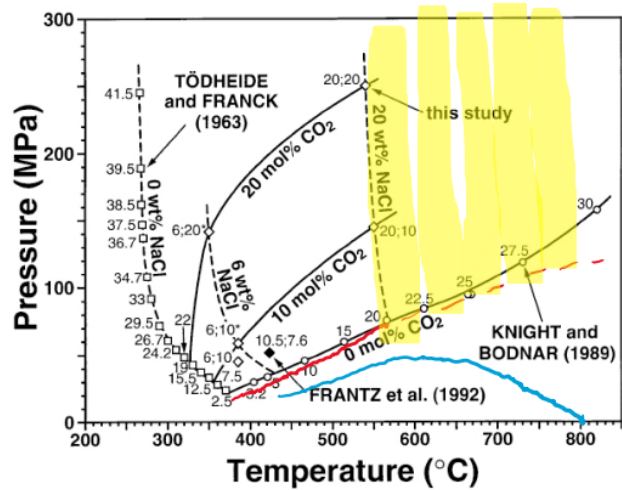
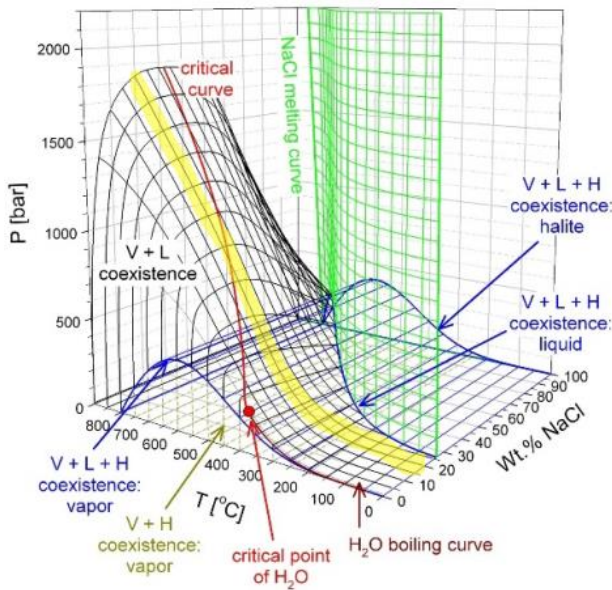
• Given the temperature range mentioned in the previous point, also both the temperatures and pressures in the middle "reservoir" are likely highly questionable.

As explained above, there is nothing questionable about the temperatures and pressures in the intermediate (middle) reservoir we estimated for the saturation decompression paths and other possible decompression paths of Solfatara fluids.

Now this in some more detail, illustrated by published figures of the respective phase diagrams.

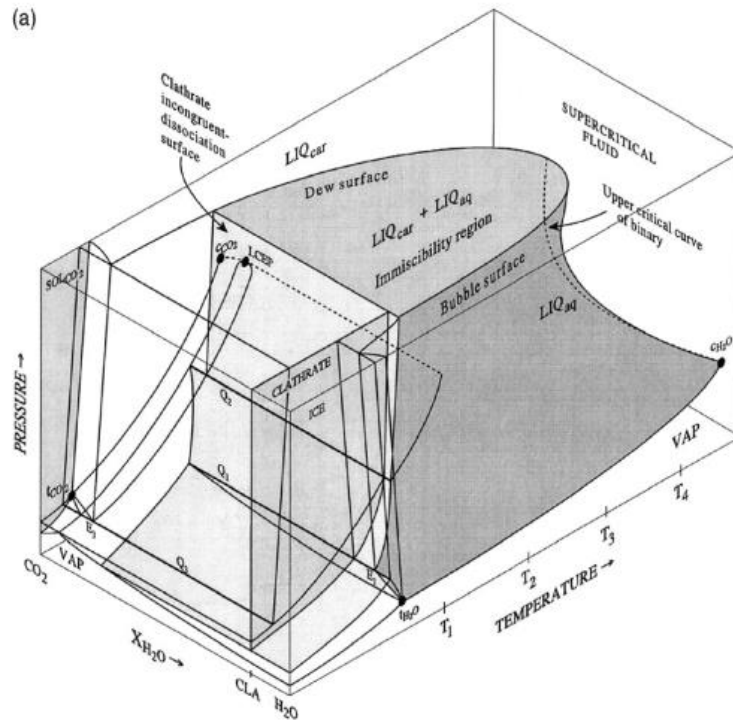
Let's start with the issue of 21% vapor-saturated brine with the diagram by Driesner and Heinrich (GCA, 2007). I have highlighted the 20 wt.% curve (let's stay with that as a convenient proxy for the author's choice for rest of the discussion) in yellow and one can see how it intersects the critical curve at ca. 590 °C, i.e., at lower temperatures it is on the liquid side of the twophase vapor+liquid surface, at higher temperatures on the vapor side. So, there is no such thing as a 20 wt% saturated liquid at temperatures higher than this. One might

now argue “ok, let’s simply take a higher salinity such as 33.5% used elsewhere in the manuscript and the problem is gone”.



Well, before we come to that point let’s first look at a relevant P-T projection of parts of the H₂O-NaCl-CO₂ phase diagram, taken from Schmidt and Bodnar (GCA, 2000). The most relevant feature in that diagram is the near-vertical line labeled “20 wt% NaCl”. This is the critical line for the pseudo-binary “20 wt% NaCl/80wt% water + CO₂”. At temperatures higher than that curve any fluid in the ternary H₂O-NaCl-CO₂ system that has a 20:80 wt% ratio of NaCl and water and has some CO₂ content will exist as a single-phase, “supercritical” fluid (highlighted yellow, extent to bottom not well known and not well understood). Red added curve is the approximate location of 20 wt% NaCl on V+L surface (solid curve: liquid, dashed curve: vapor), added blue curve is threephase vapor+liquid+halite, both in the H₂O-NaCl binary. In that binary, below the dashed red curve, there would be liquid with >20% NaCl in coexistence with a vapor <20% NaCl but no fluid phase with 20wt% can exist there. What happens below the red curve in the ternary is not well known, in particular if and where it comes to halite saturation as that is now a divariant surface in T-P rather than a univariant curve and may actually start at much higher pressures than in the binary (see, e.g., Anovitz et al., GCA, 2004).

*I think it is obvious from the above that the authors’ pressure calculation method has no foundation at temperatures above ca. 590 °C and that, therefore, **the pressure calculations for the deep reservoir are simply invalid**. An additional, very important point now is that, at the higher temperature conditions, appreciable amounts of NaCl would be present in the vapor phase (in different concentrations for different T-P) rendering the used Peng-Robinson e.o.s. version non-applicable. For example, already at 500°C and 500 bar, Anovitz et al. (GCA, 2004) found up to several mole percent NaCl in the vapor and this should be expected to increase with higher temperature for the simple thermodynamic requirement that it needs to converge with the aqueous liquid’s concentration towards the upper critical end curve. **Therefore, even the thermometry is seriously questionable for temperatures of the late part of the time series for the middle reservoir and for all temperatures of the deep reservoir.***

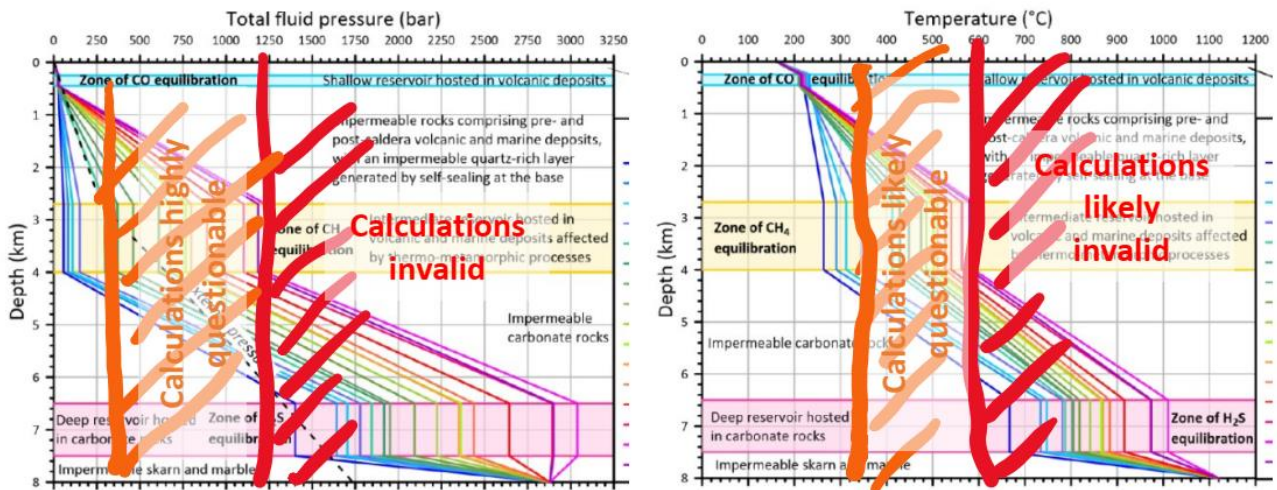


The full implications of the diagram above are nontrivial to comprehend as it is a 2D projection of elements of a 4D diagram. For me, the most intuitive and plausible image emerges when taking the H₂O-CO₂ phase diagram in 3D as a reference, e.g., from Diamond (Lithos, 2001). What is labelled there “Upper critical curve of binary” is the “0 wt.% NaCl curve” in the previous diagram, i.e., this diagram could roughly be imagined as an extension of the previous diagram to the left with X_{CO₂} as an axis going into the diagram. The “Upper critical curve of binary” limits the chimney-like carbonic-aqueous immiscibility region to high temperatures. We could imagine this as a crude guide for how the “immiscibility chimney” expands and shifts to higher temperature when moving to the pseudo-binary “20 wt% NaCl/80wt% water + CO₂” (most elements in the previous diagram): also there, it’d be a “chimney” with significant mutual solubility on the steep saturation surfaces (again: not lines) on the aqueous and carbonic sides and limited to high temperatures by the “20 wt% NaCl” line in the second diagram.

Now, this also explains why choosing saturation of a 33.5% “brine” would not do the job: although the upper critical line of that pseudo-binary would be at higher temperatures (about 1000°C) the mutual solubility would still eliminate the choice of a single saturation pressure and the saturation surfaces would still be steep, i.e., saturation pressure ranges are very large. Even worse (see also Anovitz et al., 2004, their Figure 4): at a given temperature and pressure varying X_{CO₂} of the saturated vapor will make the NaCl content of the saturated liquid change significantly. **So, the authors barometry approach also breaks down at temperatures relevant for the middle reservoir.**

Unfortunately, for the lack of more experimental data, we don’t know to how low temperatures this may be the case but I think it would be good scientific practice to cautiously assume that Anovitz’ 500°C is not a fortuitous hit of the lower temperature limit of the problem. The community has not yet fully explored and understood all the phase relations in the H₂O-NaCl-CO₂ ternary, namely on the carbonic -side or at the low pressure end. Yet, with the above (which necessarily was highly simplified and incomplete) I think we have understood enough that the negative assessment about the (in)validity of the authors’ approach is robust.

In terms of the manuscript’s main results this means graphically:



All this long discussion adds nothing to what the reviewer already pointed out above. The gist of the discussion is that the relation for a brine containing 21 wt% NaCl and the related vapor phase can be used up to 590-600°C whereas the relation for a brine containing 33.5 wt% NaCl and the related vapor phase can be used up to 1000°C, with more uncertainties. Anyhow, the CH₄ equilibrium temperature which refers to the intermediate reservoir are generally lower than the 600°C threshold and moderately higher in few cases while the H₂S equilibrium temperature which refers to the deep reservoir are generally lower than the 1000°C threshold and moderately higher for few samples. **Again, the reviewer confuses the two temperatures and the two reservoirs.** Nothing new apart from the two diagrams defaced by childish graffiti and scribbles which are ethically questionable.

To add on this: the authors could have suspected a serious problem already from their pressure diagram. Fluid pressures as high as 2.4 times lithostatic (or, in absolute values overpressured by up to 1800 bar) and fluid pressure gradients similarly excessive, in particularly in the hot, ductile regime, would be considered unrealistic by many (if not most) people dealing with such problems for reasons laid out, e.g., by Cox (Geofluids, 2010) or discussed in the Weis et al. (2012) paper (or follow-ups on that) that the authors considered not relevant in their rebuttal. In essence, (ductile) rocks cannot sustain such high fluid overpressure, the values are very unrealistic. Since a lot of the implications of the model hinge on that, the author may want to acquaint themselves more with rock failure related to fluid pressure (the Cox paper is a good introduction).

Although in the reviewer’s words we clearly perceive a certain ethically-inappropriate sarcasm and a lack of respect towards us, we appreciate the reviewer’s suggestions to acquaint ourselves more with rock failure related to fluid pressure. We believe there is always something to learn. Nevertheless, we are not totally ignorant on this subject because we have gained some experience by working on the brittle-ductile transition in the Tuscan geothermal systems (e.g., Marini and Manzella 2005). As a matter of fact, the knowledge of these systems gained through multidisciplinary surface exploration and drilling of geothermal wells to depths of almost 4 km allows one to understand the rheological behavior of rocks quite realistically.

Now, to be “constructive” after all this: The phase relations discussed above also propose a possible way how the “middle reservoir” can indeed be the source of bradyseism. If the fluid released at depth were a “supercritical” H₂O-NaCl-CO₂ mixture then upon decompression it may hit the “immiscibility chimney” displayed in the CO₂-related phase diagrams above. For a suitable parameter combination this should result in sufficient pressurization.

Similarly, the overpressure problem goes back to the assumed temperature-pressure “saturation decompression path” and the fact that it is simply arbitrary, not founded on any data or defensible theory, and leads to too high pressures. Given the above discussions on the phase diagram it seems likely to me that

a plausible decompression path can be constructed that implies lower, or [more] realistic pressures at depth. Then, “lithostatic plus a defensible overpressure” in the deep “reservoir” would be a good starting point for revising the decompression path (from the source upward rather than vice versa) of the “revised conceptual model”.

We thank the reviewer for this suggestion but we prefer to keep our interpretation.

Up to here, I consider this reply as essential information for the editor. I hope the explanations are not “too nerdy” to be evaluated for the decision process (if they are, please request an explanation in simpler words) and I hope that also the authors can accept my criticism given their own statement “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”. I think I clearly showed above that the study contains serious problems of both kinds.

We think we clearly showed above that the review contains serious problems of scientific validity and is affected by several errors.

In the following I take the freedom to share some reflections with the authors as on what other aspects I think they may want to consider and/or re-think when re-visiting their model. This will also reply to some selected parts of their rebuttal. I will not answer to all points as I think that the discussion has already reached a point of getting lost in unnecessary back-and-forth. I don't claim to own the truth here but I would expect my thoughts to be considered a bit more seriously (1) as possibly valuable when revisiting the model and (2) for what to pay attention to beyond the gas chemistry point of view.

We are open to consider respectful and scientifically valid critiques. However, point (2) written above (“for what to pay attention to beyond the gas chemistry point of view”) is not correct because we considered different geoscientific data, whereas the previous part of the review was focused on the H₂O-NaCl-CO₂ ternary and related binaries almost exclusively, apart from a few considerations on rock rheology (see above).

Various points

- As an add-on to the discussion above, I would like to suggest to the authors to also think a “decompression path” indeed from the deep source upward and not top down from the surface (which is rather a “pressurization path”) although the gas data were collected there. Phase changes will modify CO₂-H₂O ratios upon ascent and the degree and cause of this modification cannot be quantified in the top down way; e.g., for your shallow isenthalpic paths, for example, when going down you hit the H₂O-CO₂ saturation on the (carbonic) vapor side (on a rather flat surface that forms the “chimney’s” bottom; such vapor can be equally well result from temporary saturation and condensing out some minor liquid (due to the “bulge” in the vapor enthalpy curve as you discussed) or from the (boiling-like) exsolution of a mass-wise minor vapor phase from an CO₂-poor but mass-wise dominant aqueous liquid. What happens below that saturation depth is, therefore, ambiguous and cannot be constrained from surface data as presented. Also, for this problem, I missed a clear statement of what your assumptions were for the top down approach regarding the fluid phase evolution with depth. Such a statement would have allowed readers/reviewers to test your hypothesis; leaving it out – or not at least discussing this / not formulating a hypothesis – is not good practice.

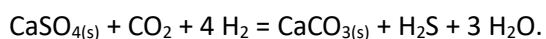
Since the gas data were collected at the surface, we think that the top-down approach (using the reviewer's words) is more suitable than the opposite bottom-up approach. If one wants to consider the effects of partial water condensation (as done in some papers of Chiodini and coworkers), it is necessary to introduce an assumption which cannot be tested. So, we prefer to use the analytical data without any correction to avoid to complicate the problem rather than to simplify it. Furthermore, in the book we considered also the chemical kinetics of the reactions involving H₂O, CO₂, CO, CH₄ and H₂, which has been the subject of several studies, and we applied a simplified reaction path model, simulating the heating of the Solfatara fluids

collected at the surface. The equilibrium temperatures computed by the reaction path model compare with those given by simple gas geothermometers, within acceptable differences. Thus, gas geothermometers work well, at least for the intermediate reservoir.

- Again on top down vs. bottom up: that was also the main reason for recommending Einaudi et al. and others for sulfur or Weis et al. for thermo-hydrology. I did not assume that the former were up to date with respect to the latest in volcanic gas chemistry but these papers think the chemical (or fluid flow, respectively) process from the source to the surface and this clearly adds value. Namely, Einaudi et al. highlight that the fluid passes through different redox and fS₂ conditions along its path as exemplified by successive mineral assemblages observed, which will, among others, also alter sulfur speciation and fugacity/concentration (and therefore the values of your H₂S thermometer) on the way up. To me this looks geologically and geochemically much more logically and advanced than the assumption of a single mineral-fluid reaction fixing it right away at 7 or so km depth. Whether the Weis model was inspired by porphyry deposits doesn't play a role; to me, it models a generic magmatic fluid release process that was then interpreted by those authors for its relevance for porphyry-Cu deposits.

- A bit more about the reactive path of sulfur: for the deep parts, the main window of action for SO₂ + H₂O reacting are believed to be below 500ish °C or so (gas redox buffer followed by disproportionation along cooling path, if I remember correctly). This is at lower temperatures than your H₂S thermometer equilibration and should therefore be assessed for a possible impact on H₂S concentrations on the way to the surface.

We have nothing to add to our previous rebuttals to these reviewer's considerations apart from a comment on H₂S, in that possible reactions causing significant changes of this gas species were considered in the book. The fugacity of gaseous S₂, SO₂ and COS were computed as a function of the CH₄ equilibrium temperature (called SS4 equilibrium temperature in the book) and resulted to be negligible. We have also considered the pyrite-pyrrhotite, pyrite-fayalite-quartz, pyrite-magnetite, and pyrite-hematite equilibria, but the computed equilibrium temperatures have no physical significance, suggesting that the H₂S concentration of Solfatara fluids is controlled by other reactions. Considering the presence of carbonate rocks at depths from ~ 4 km to ~7.5 km, we assumed that this reaction is:



- Fournier vs. Weis et al.: the Weis model replaced the Fournier concept in that it explains the lithostatic to hydrostatic transition as a natural consequence of degassing magmatic fluids having the dual role of heating the rock overlying the magma to ductile temperatures and impermeable behaviour and, in turn, of transiently breaking those heated rocks due to pressure build-up to allow the temporary release of fluids; this magmatic-hydrothermal domain than naturally transitions into a classical geothermal system further up; there is no need for self-sealing by silica, just heat + fluids do the job already, matching many features of natural systems (fossil or active). Let Occam's razor do its job here.

We prefer the Fournier model also considering the occurrence of quartz in the deepest section of geothermal well San Vito-1.

- Lupi/Weis: well, that was quite a cheap trick referring to what I did not point at (the trigger mechanism, which indeed can be questioned) and then trying to make me look ridiculous by criticizing that. However, I appreciate that you didn't fully lose humor over my review. I was pointing at the overpressure waves rising in the magmatic-hydrothermal plume and these – if I remember that correctly from in-depth discussions with Weis – happen on time scales of years or 10s of years; i.e., they are highly relevant. Furthermore, you could learn from Weis et al. how H₂O-NaCl phase relations (unfortunately, no CO₂) evolve with space and time in such a system to come back to the main problem of your calculations.

It was not our intention to do cheap tricks and make ridiculous the reviewer. We are interested in scientific aspects only. We are convinced that the overpressure waves rising in the magmatic-hydrothermal plume does not provide a reasonable explanation of the on-going unrest phenomena at Campi Flegrei.

- It were these last few points that made me make the comment on “apparently from a volcanology background” as the way the manuscript is written it reads like a naive “what comes out of the fumaroles is what is at depth”. There is nothing about “second class scientists” implied but rather should highlight the impression of a surface data-biased view on fluid processes in the deep parts of magmatic-hydrothermal systems (btw. understood as systems dominated by magmatic fluids). A lot of valuable information on the latter is available (mostly from the economic geology community) that could have informed the conceptual model design with quite some advantage but was not considered. In hindsight, I admit that the statement could be misinterpreted and hope these remarks clarify that.

We thank the reviewer for clarifying the comment “*the authors (apparently coming from a volcanology background)*” in the previous review.

- Convective zero temperature & zero gradient pressure profiles: another one that was apparently intended to make me look like a beginner by referring to an introductory book. My point was that your “convective” vertical temperature profiles in the reservoirs are an ad hoc invention based on no data and should, therefore be declared as such or be justified. BTW: zero pressure gradient vaporstatic columns would not convect. Regarding that zero pressure gradient, for the fun of it, let’s take you own data, for example the Oct10-Jun12 H₂S equilibration conditions: a pure water vapor at 830 °C and 2157 bar would have a density of 432 kg/m³. In the CH₄ equilibration reservoir for the same period one would have 412 kg/m³ [kg/m³]. This is >0.4 times a cold hydrostatic gradient, far away from zero gradient. So, no point to make me look ridiculous when your own data proof you wrong. In my group it is a routine process to perform such obvious checks before adding conceptual figures to a publication.

First of all, we did not intend to make the reviewer look like a beginner by referring to the textbook by Malcolm A. Grant and Paul F. Bixley (2011) Geothermal Reservoir Engineering, Second Edition; we referred to this textbook because it is the most suitable reference in geothermal reservoir engineering. Second, the vapor-static column convects as discussed in the papers quoted in our previous reply as well as in the textbook by Malcolm A. Grant and Paul F. Bixley, which evidently the reviewer ignores. Third, the zero-pressure gradient is typical of vapor-dominated geothermal systems at temperature and pressure close to the point of maximum enthalpy of water vapor (235°C, 30.6 bar). In contrast, the intermediate and deep reservoirs of the Solfatara hydrothermal-magmatic system are generally at temperatures and pressures much higher and have densities relatively high making the pressure gradient in the intermediate and deep reservoirs higher than zero. The reviewer is absolutely right on this point. Nevertheless, it is not correct to consider the densities of pure water vapor, as done by the reviewer, due to the presence of significant gas amounts, mainly CO₂, in the gas mixtures of interest. We have revised Figure 6 (which will be presented in the revised version of the manuscript), showing the time changes, between September 1984 and January 2022, of the total fluid pressure vs. depth profile along a hypothetical borehole drilled in the Solfatara crater. For the vapor in equilibrium coexistence with a brine containing 21 wt% NaCl, we have considered the molar volumes reported in Tables 1, 2, 3, 4, and 5 of Chapter 9 of Marini et al. (2022), whereas for the vapor in equilibrium coexistence with a brine containing 33.5 wt% NaCl, we have considered the molar volumes reported in Tables 9, 10, 11, 12, and 13 of Chapter 9 of Marini et al. (2022). The obtained log-densities in log-kg/m³ were then fitted against X_{CO2} and temperature to derive simple polynomials that were used to calculate the density of the gas mixtures in the intermediate and deep reservoirs, which were assumed to be constant to avoid complicating too much the calculations. Knowing the density, ρ (in kg/m³), the total fluid pressure at the bottom of the two reservoirs of interest, P_B (in bar), was computed, to a first approximation, by the relation:

$$P_B = P_T + 1000 * \rho * g * 0.00001$$

where $g = 9.80665 \text{ m/s}^2$ is the conventional standard value of the gravity acceleration. Again, we do not intend to make the reviewer look ridiculous, but the data we used are not wrong. Our previous Figure 6 had minor inaccuracies which were adjusted as explained above. If the reviewer intends to build a case on these minor inaccuracies, we cannot stop the reviewer.

We are pleased to know that, in the reviewer's "*group, it is a routine process to perform such obvious checks before adding conceptual figures to a publication*", but these checks should be done using the proper data, not using improperly selected data, that is, neglecting the presence of gases and referring to pure water. For instance, the density value of 431.61 kg/m^3 at $830 \text{ }^\circ\text{C}$ and 2157 bar and the density value of 412.12 kg/m^3 at $468 \text{ }^\circ\text{C}$ and 582 bar pertain both to **supercritical pure water**, while we are dealing with a vapor in equilibrium with a brine containing 33.5 wt\% NaCl and a vapor in equilibrium with a brine containing 21 wt\% NaCl , whose density values are 430.35 and 289.39 kg/m^3 , respectively, according to our approach. Even worse, if one considers the September 1984 – April 1987 period, with $264 \text{ }^\circ\text{C}$, 56.7 bar in the intermediate reservoir and $667 \text{ }^\circ\text{C}$, 1401 bar in the deep reservoir, the computed density values for the pure water system, 778.18 and 416.23 kg/m^3 , respectively, refers to **pure liquid water** [sic!] and again to **supercritical pure water**, respectively. In contrast, the density values are 32.95 and 383.71 kg/m^3 , respectively, according to our approach.

- "inferred geology". Let me cite the book, page 40: "In particular, according to Zollo et al. (2008), the *inferred* schematic stratigraphy comprises, from top to bottom (Fig. 10):". So, please don't bash me if I use your words.

In our previous rebuttal of the reviewer's critique on this point we wrote that "*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.*" It is true that the stratigraphy was inferred by Zollo et al. (2008) based on the active seismic reflection data acquired by the SERAPIS survey. But this is how geophysics works. We did not add any inference.

- Calcite-H₂S: you are right, geology rules. I should have expressed much clearer that I was referring to the effect of reactive transport on sulfur content. There, I don't agree that the absolute concentrations don't matter because small concentrations may easier experience massive relative modification (reactive transport is always a competition between equilibrium constant and actual masses present) than bigger ones. Side remark, lines 69-71 of rebuttal: there is no such thing as a "strong acid" at those conditions; acids known to be strong at ambient conditions become weak in the low dielectric constant aqueous solvent at those conditions. As illustration: according to Supcrt, if one trusts it, the $\log K$ for $\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+$ in the temperature range of 500 to $800 \text{ }^\circ\text{C}$ and densities from 0.4 to 0.6 g/cm^3 is in the range of -8 to $-11 \dots$

We agree that "*there is no such thing as a "strong acid at" the conditions of the deep reservoir; "acids known to be strong at ambient conditions become weak in the low dielectric constant aqueous solvent at" the high temperature, high P conditions of the deep reservoir.* We know very well the decreasing dissociation of acids with increasing temperature (e.g., Marini et al. 2003 a, b; Marini and Gambardella 2005). Side remark: the reviewer used again SUPCRT92, whose thermodynamic database refers to pure water, doing the same mistake done in density calculations.

- Finally, I think my doubts about the compatibility of "reservoir" and equilibration and a structural transport highway remain valid but there is no point discussing this further here. This applies also for all other points I may not have responded here, too.

We hope that our responses to the specious and unconstructive criticisms advanced by the reviewer will help to demonstrate the validity of our work, at least to those who read and comment on it with an open mind, not clouded by prejudice. Unlike the reviewer, who intends to end the discussion, we are willing to continue it as long as it is deemed necessary.

I would like to conclude with stating that I start to appreciate the egosphere discussion format. Although I was annoyed by the extra effort compared to what it could have been if the manuscript were properly prepared, I think such discussions can be very helpful and help bridging gaps between different communities, one of which became very obvious here.

We would like to emphasize once again that the reviewer used the EGU sphere public discussion format only for specious and unconstructive criticism not only on our manuscript, but also on our book. Of course, everyone is free to judge books as they prefer, but let us say that we perceived the reviewer's criticism of our book as a deliberate and unsolicited personal attack. The extra effort implicit in the review of our book is a rather obvious consequence of this choice of the reviewer, since the task assigned to the reviewer was only the scientific review of the manuscript. Finally, we agree with the reviewer on at least one thing, namely the usefulness of the EGU sphere public discussion format. Nevertheless, when one participates in a public discussion, she/he should have the good manners to reveal herself/himself and not to hide behind anonymity, even if it is permitted by the reviewer role.

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