

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.

### ***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 sub-areas 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).

**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 H<sub>2</sub>O-NaCl binary and adding a simplistic pressure correction for the presence of CO<sub>2</sub> in the vapor phase (as a side remark I wonder how one could call that “in *equilibrium* with a brine”; but see discussion of CO<sub>2</sub> 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).

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 H<sub>2</sub>O-NaCl system<sup>1</sup>), so the calculation is meaningless for all inferred temperatures for the deep “reservoir” and for the hottest of the middle one.
- Instead, above that temperature, an H<sub>2</sub>O-NaCl fluid on the twophase 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 H<sub>2</sub>O-NaCl-CO<sub>2</sub> system is nearly isothermal at those 590 °C: if CO<sub>2</sub> is present, the fluid at such high temperature and pressure conditions would be a homogeneous, “supercritical”, dense vapor-

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<sup>1</sup> 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.

- 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.
- 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.
- Moreover, the approximation of a carbonic vapor phase pressure in “equilibrium” with a vapor-saturated H<sub>2</sub>O-NaCl liquid is only acceptable if the mutual solubilities of CO<sub>2</sub> 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.

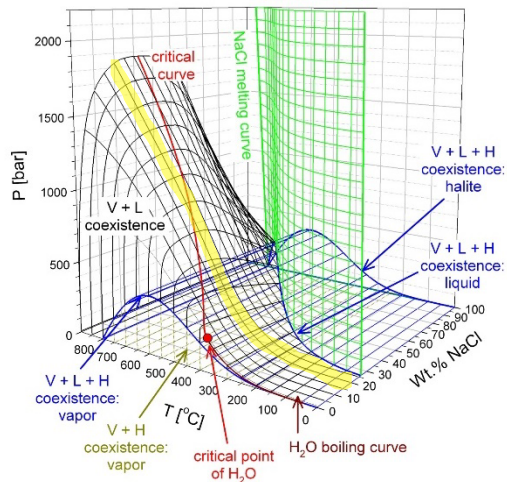
This holds true for typical geothermal systems at less than ca. 300ish °C and has, therefore, indeed be applied to such systems. As soon as the mutual solubilities are non-negligible (starting at T > ca. 300ish °C, some people might claim 350ish °C, it really doesn’t matter much) this is not possible 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<sub>2</sub> 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<sub>2</sub>” instead of a single saturation line. Side remark: so much about the authors’ statement “there is no need for an *adequate solubility model for the gases in such a brine*.”

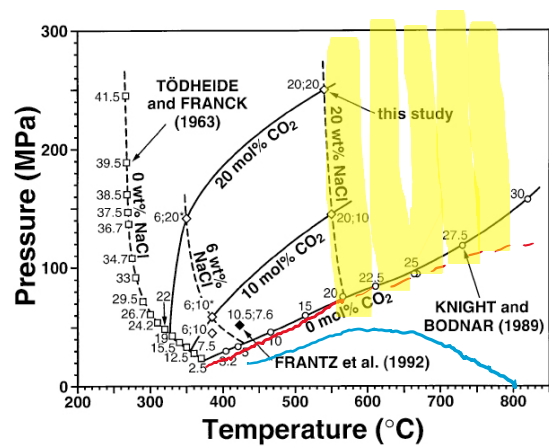
- Given the temperature range mentioned in the previous point, also both the temperatures and pressures in the middle “reservoir” are likely highly questionable.

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”.

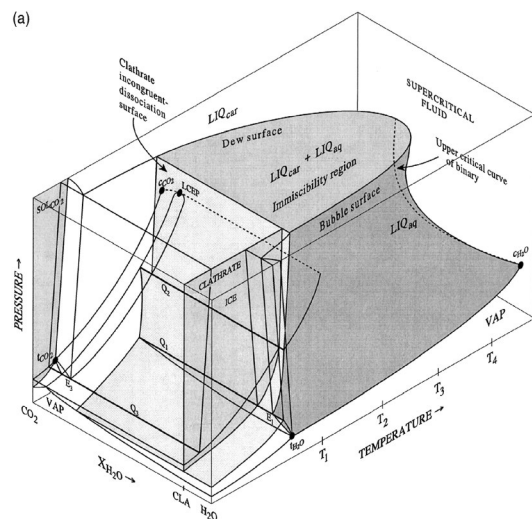


Well, before we come to that point let's first look at a relevant P-T projection of parts of the H<sub>2</sub>O-NaCl-CO<sub>2</sub> phase diagram, taken from Schmidt and Bodnar (GCA, 2000). The most relevant feature in that diagram is the near-vertical line labeled "20 wt% NaCl". This is the critical line for the pseudo-binary "20 wt% NaCl/80wt% water + CO<sub>2</sub>". At temperatures higher than that curve any fluid in the ternary H<sub>2</sub>O-NaCl-CO<sub>2</sub> system that has a 20:80 wt% ratio of NaCl and water and has some CO<sub>2</sub> 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 H<sub>2</sub>O-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 non-trivial 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 H<sub>2</sub>O-CO<sub>2</sub> 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<sub>CO2</sub> 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

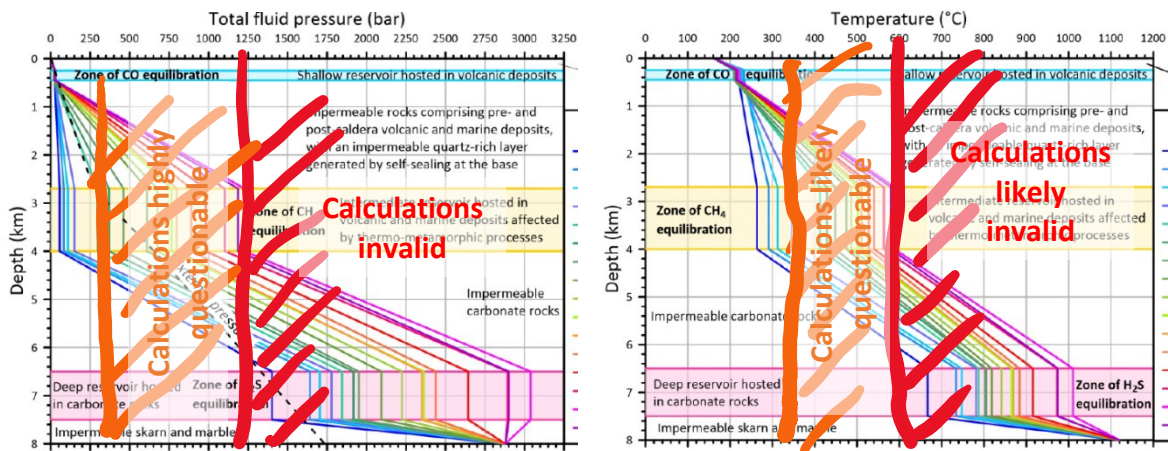


to higher temperature when moving to the pseudo-binary “20 wt% NaCl/80wt% water + CO<sub>2</sub>” (most elements in the previous diagram): also there, it’d be a “chimney” with significant mutual solubility on the steep saturation surfaces (again: not lines) on the aqueous and carbonic sides and limited 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<sub>CO<sub>2</sub></sub> 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 H<sub>2</sub>O-NaCl-CO<sub>2</sub> 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:



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).

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” H<sub>2</sub>O-NaCl-CO<sub>2</sub> mixture then upon decompression it may hit the “immiscibility chimney” displayed in the CO<sub>2</sub>-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, 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”.

***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.***

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.

### ***Various points***

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- 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 CO<sub>2</sub>-H<sub>2</sub>O 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 H<sub>2</sub>O-CO<sub>2</sub> 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 CO<sub>2</sub>-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.

- 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  $f_{S_2}$  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  $H_2S$  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  $SO_2 + H_2O$  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  $H_2S$  thermometer equilibration and should therefore be assessed for a possible impact on  $H_2S$  concentrations on the way to the surface.
- 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 then 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.
- 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  $H_2O$ -NaCl phase relations (unfortunately, no  $CO_2$ ) evolve with space and time in such a system to come back to the main problem of your calculations.
- 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.

- 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 your own data, for example the Oct10-Jun12 H<sub>2</sub>S equilibration conditions: a pure water vapor at 830 °C and 2157 bar would have a density of 432 kg/m<sup>3</sup>. In the CH<sub>4</sub> equilibration reservoir for the same period one would have 412 kg/m<sup>3</sup>. 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 prove you wrong. In my group it is a routine process to perform such obvious checks before adding conceptual figures to a publication.
- “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.
- Calcite-H<sub>2</sub>S: 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 logK for HSO<sub>4</sub><sup>-</sup> = SO<sub>4</sub><sup>2-</sup> + H<sup>+</sup> in the temperature range of 500 to 800°C and densities from 0.4 to 0.6 g/cm<sup>3</sup> is in the range of -8 to -11 ...
- 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.

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.