Many thanks for your excellent and forgiving review of my first version of this manuscript. I have attempted to respond to every point raised, and will go through them individually.

Several comments are shared between reviewers, and in these cases I respond in the first instance they are raised (e.g. by Reviewer 1) and refer back to this response on subsequent occasions.

The fundamental issue raised during review was the robustness of the methods we had used to generate our result. This point is of such fundamental importance, we elected to seek the assistance of a colleague in our Chemistry Department (Dr. Jay Wadhawan) who specialises in solution chemistry. Dr. Wadhawan has reviewed our methods and provided better and more elegant solutions to a number of points. We feel this has improved the study considerably, and hope you also find it both more robust and more clear this time.

Editor Comments

1.1) **Incorrect equation, and uncertainty about the Gibbs Free Energy concept.** The equation was indeed incorrect, for which we apologise. Mathematical issues are resolved in our responses to Reviewer 1. The way we conceptualise excess Gibbs Free Energy throughout this study is to consider the amount of free energy represented by an amount of substance held in a particular aqueous solution. The amount of free energy can be written as below (Eq. 1.18 from Langmuir, 1997).

$$G_A = \Delta G_A^o + RTln[A]$$

The idea that a system can "have" a free energy level is therefore acceptable within a standard thermodynamic framework. At equilibrium, a reaction involving 2 substances can be represented as (Eq. 1.21 from Langmuir, 1997)

$$\Delta G_r = -RTln\left(\frac{[A]^a}{[B]^b}\right) = -RTlnK_{eq}$$

For a solution, it can be rewritten

$$\Delta G_r = -RTlnK_{sp}$$

The chemical potential form of this behaviour (i.e. for a system out of equilibrium) will then be (derived from Langmuir, 1997, Eq. 1.26).

$$\Delta G_r = RTln\left(\frac{IAP}{K_{sp}}\right)$$

Where IAP is the Ion Activity product.

1.2) **"Antiquated" equation, and the use of PHREEQC.** We have used an equation from one of the recommended sources as requested, although we do point out that the new relationship (Davies) is in fact an approximation to the original equation we used (Robinson-Stokes). We have also amended our argument concerning our preference for an analytical solution. We feel that the discussion that has happened regarding our analytical solution – and the

improvements this has led to us making – strongly emphasises the advantages of this approach. Everything is in the open, and available to the reader for debate and criticism.

1.3) **Use of SNI.** The way we computed and used SNI previously clearly caused confusion and concern. We have reconsidered the original strategy, and now provide relative Gibbs Free Energy values rather than converting to SNI. We have removed our use of the terms entropy and enthalpy, and use more descriptive language now.

We emphasise, however, the problem we are trying to solve is inherently very complex, and difficult to conceptualise. If we had confidence that the Editors view of the system being driven by degassing was correct, we could simplify it – but we do not. The driving force for precipitation could be outgassing or indeed ingassing, which is well accepted - particularly in anthropogenic sites (Andrews et al., 1997). Ionic strength is key to many calculations, so precipitation of non calcium or carbonate bearing mineral phases could be key in some sites. Mixing could be key, especially where thermogenic solutions interact with karst groundwater which generally has low ionic strength but moderate calcium and carbonate concentrations. Even beyond this, other effects - inorganic and organic - could be considered. Given all these influences, it is impossible to attach the generation of the chemical potential of the system to undergo a spontaneous change (the relative Gibbs free energy) to a single process or reaction is impossible. The important thing for our study is not how the chemical potential arises, it is that it exists.

2.1) Introduction. We have expanded the section identified, and we hope this is clearer and more useful to non specialist readers now.

2.2) Issues with figures and tables. We have fully revised, and mostly redrawn, the figures and tables. We hope these are now much improved.

2.3) Do we mean desorption? We have replaced the word with "degassing". **Cation.** We have changed this. **Physico-chemical.** We have also changed this. **Non-tectonic?** We are attempting to refer to those systems not reflecting deep-crustal processes. We have now reworded this sentence.

3) Summary. We did indeed find all the comments extremely helpful and thought provoking, and thank both Reviewers and the Editor for the hard work they have done on our behalf.

References

Andrews, J. E., Gare, S. G., and Dennis, P. F.: Unusual isotopic phenomena in Welsh quarry water and carbonate crusts, Terr. Nova, 9, 67-70, 10.1111/j.1365-3121.1997.tb00004.x, 1997.