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Interactive comment on "Linking process and product in terrestrial carbonates using a solution thermodynamic approach" *by* M. Rogerson et al.

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

Reviewer 1 - Adrian Immenhauser

1) Title is unclear. We have altered the title to “Linking mineralisation process and sedimentary product in terrestrial carbonates using a solution thermodynamic approach.” We hope this now more clearly expresses what we are trying to achieve.

2) Oncoids and use of the term “discontinuous”. Oncoids are laminated, microbially precipiated, millimetre to centimetre diameter spheroids which grow under turbulent conditions at the sediment/water interface and have laminae constructed of sparitic, thrombolitic or micritic carbonate, or an alternation of more than one. Although oncoids were indeed originally described from the marine realm (Peryt, 1983; Riding 1991) they are also common in ambient (Pedley 1990; 2009) and thermal freshwater (Chafetz et al., 2003; Jones et al. 1998) situations and can routinely be found in carbonate-rich surface water systems.

Tufa laminae are indeed often discontinuous on a meter scale, although they tend to extend at least over tens of centimetres if not many meters. For this study, we are primarily interested in tufa beds however, and these may be meters thick and can routinely be many tens of meters in lateral extent. At their largest, oncoids are a few centimetres in diameter, and so carbonate deposition on the scale of a tufa bed is highly discontinuous between individual oncoids. Even within an oncoid, successive laminae are often discontinuous on a finer scale than found in tufa laminae. This is caused during occasional circumrotatory motion under higher energy conditions, but may equally be due to unequal surface growth when part buried in the substrate. It is therefore fair to describe tufa as a more continuous style of deposition than oncoid carbonates.

3) Focus on geomicrobial processes rather than inorganic ones. We recognise this is not only a controversial point, but is simultaneously a point that has been made frequently over the years. Resolving this controversy is long overdue, and this - in itself – justifies our argument that in the immediate future, focus must be on geomicrobial processes. In this study the difference we attempt, hopefully with some success, to understand the relevent inorganic processes analytically. We are at least ten years from

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achieving that level of understanding in the geomicrobial realm. Again, this emphasises where future research focus has to be concentrated.

We have included more references into the introduction, including to Bruce Foukes seminal Yellowstone studies.

4) Equation on p. 439 ln. 3. This equation was incorrect! It is correct in my Word version, and has clearly been mangled during creation of the pdf. This is very embarrassing, and I certainly should have noticed this during proof reading. I am very impressed that despite this basic error, 2 Reviewers and an Editor were committed enough to plough on and see that the paper had at least some merit – for this I thank you again! We now provide a reference to Langmuir 1997, where the equation does appear.

5) A Omega; state vs index. Due to the revision of our approach, Omega no longer appears. B What does Ksp denote? Ksp is solubility product. We have ensured this is correct throughout.

6) Calculation of Omega. Again, this calculation no longer appears due to a different mathematical approach.

7) Calculation of activity coefficients. Following the guidance of the Reviewer, we have replaced the Robinson-Stokes representation with the Davies approximation of the same behaviour. The approximation occurs in Langmuir 1997, on page 132.

8) Should units be C or J? The electron volt is no longer used.

9) Origin of equation. On the advice of Dr. Wadhawan, we have replaced this representation with an analytical solution. The derivation of the new solution is provided in the new Appendix 1.

10) Stoichiometic calcite? All approaches do indeed assume stoichiometric calcite, as they would using standard aqueous geochemical models like PHREEQC. This is because it is difficult to resolve issues involving specific ion-mineral interactions when

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we have such a range of ions potentially present within the sum of all the systems studied. We emphasise that not only is there clear inorganic "dirtiness" to consider, organic molecules are well known to bind onto crystal surfaces and "poison" their growth (Decho, 2010). We could attempt to discuss the influence of all of these influences in isolation, speculate about their impact in combination and drawn some general conclusion. But this would probably double the length of the manuscript. Possibly, this is a challenge we should aim to address?

We no longer use SNI, but report the relative Gibbs Free Energy value directly, and the methodological approach we use can now be directly traced to Langmuir 1997 to assist non-specialist readers (see response to Editor). Although the new representation changes the absolute values in Figure 3, it does not alter the structure of the dataset.

11) Do not use the terms enthalpy and entropy. We have done as recommended.

12) Case examples: We have revised and simplified the text in this section, to make it easier to follow. A full dataset is now available in Appendix 2. We do not think it is appropriate at this stage to undertake a classification of all these systems or datapoints, however. This is because we deliberately do not attempt to identify "hard" divisions between classes. The data used in our study is necessarily limited, and a bigger, more global dataset should be created before the boundaries of classes are firmly identified.

13) Figure 8a. You are correct – we have amended this.

14) Oncoids. See point 2. We have added additional text and references here, emphasising that there is quite a rich literature on terrestrial oncoids dating back at least to the 1980's. They are oblate in the strictly geometric sense, in that their horizontal axis is always considerably larger than their vertical axis.

15) Table 3 is a mess. We have cleaned it up.

16) Table 2 is also a mess. We have also cleaned this table up.

17) Logarithmic scales? Correct, we have amended.

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18) Problems with Figure 3. We have ensured symbols for different systems are different, and corrected the issue with the axis labels. Italian and Turkish data are indeed all given the same 2 symbols, despite being sub-divided in the summary table. However, the classification in Table 2 is done on the basis of temperature and, thus is easily applied to Figure 3. We have indicated the divisions on the upper part of the diagram.

19) Figure 4 D and E. Reference to D and E have been removed.

20) Stromatolite microherm is controversial. Nevertheless, this is the correct term for this deposit.

21) White rectangle in top left corner. Has been removed.

22) Scales and labels for Figure 11 C and D. We have improved this.

References

Decho, A. W.: Overview of biopolymer-induced mineralization: What goes on in biofilms?, Ecological Engineering, 36, 137-144, http://dx.doi.org/10.1016/j.ecoleng.2009.01.003, 2010.

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