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

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Dear editor,

Thank you for providing me with the opportunity to read the interesting ms “Linking process and product in terrestrial carbonates using a solution thermodynamic approach” by authors Rogerson, Pedley and Kelham. I apologize for the rather slow response but I indicated from the very beginning, that I would be out-of-office for quite some time. I approach this paper from the viewpoint of a carbonate geologist with a mainly field and geochemical perspective. I must emphasize that my main interest is mainly with cave carbonates rather than with tufas/travertines. I am sure; other reviewers will correct me where I go wrong. This paper struggles with the longstanding problem of carbonate depositional environments situated at the interface between chemistry,
physics and biology.

In essence, I welcome this paper and find this a valid approach towards an improved conceptionsal understanding of the significance of each of these main groups of parameters. The focus is on continental freshwater carbonate deposits summarized under the labels travertine or tufa by many. The authors lament on the lack of a comprehensive terminology in order to implement biofilm processes on carbonate precipitation. I recent listened to people talking at conferences stating the same. Hence, I conclude, the community seems to agree that they need a better terminology. Following a general introduction that is – in my view – rather well written, the authors comment on the problems posed by using literature from different communities (physical versus sedimentological in their terminology). What then follows is a brief summary of the state-of-art dealing with (micro-)biological and gel-related processes affecting (or acting as template/substratum) for carbonate precipitation. The next chapter then deals with the methods and source data and here, as I will detail further below, come most of my questions. A subsequent important chapter of the paper then deals with a – in my view intelligent – subdivision of different depositional systems using fluid temperature and the degree of biological influence and nucleation indices as main dividing factors. Reading the paper carefully, I noted quite a number of problems and inconsistencies.

Below I list my points of criticism using page and line numbers.

1. Title: Not clear to me. I assume you refer to “carbonate deposition” or “carbonate depositional environments”? If not, what is the process and product of a carbonate? I guess the carbonate is the product, hence product of a product? Confusing! Please explain. See also first line of abstract.

2. Abstract, Ln. 24 and other places in paper: The term oncoid originally comes from the marine carbonate domain and has a complex story. I would not use this label here without a proper definition. Please also explain why tufa deposition is expected to be continuous and oncoidal deposition is expected to be discontinuous? I expect tufas to
be riddled with hiatal surfaces (seasonal and beyond) and hence discontinuous.

3. Abstract, Ln. 5-6. Focus on geomicrobial processes rather than inorganic solution chemistry. Yes and no. First of all, this has been said many times before (go and take the textbook of Konhauser to start with). Hence, yes I agree. No, I disagree because both domains microbial and inorganic ones are of significance. Often, microbes lower thermodynamic boundaries but they do not alter the process as such. Take the work of Bruce Fouke in Yellowstone as an example. I fully agree with you that this is a complicated matter (see also your comments on page 347, Ln. 6 etc.). I find the cited references here incomplete.

4. Methods and source of case study data, p. 349, Ln. 3: We looked up the original equation in Dandurand et al. (1982) and tried understand what you did here? We failed. Can you please explain how your equation on Ln. 3 is related to the one in Dandurand et al. (1982)?

5. Same page, Ln. 6: To our knowledge, Omega denotes the saturation STATE not index. Please explain.

5. Same page, Ln. 20. We are lost. How do you produce this equation? Also, in our opinion, but we might be wrong, Omega is commonly expressed without a logarithm, while the saturation index is expressed as log10(x) not as ln? Please explain.

6. Same page, Ln. 23: We think that ksp denotes the activity product and not the saturation coefficient. Please explain.

7. Page 350; Ln. 2: We are confused. In our view, A in the equations 4 and 5 would refer to ion size parameter and NOT to bond lengths. Furthermore, far less complicated equations for alpha and beta exist. Also the cited work of Robinson and Stokes (2002) is a reprint of a classical book from 1970 lacking a serious update as far as I am concerned. More recent work is found in Langmuir (1997; Aqueous environmental geochemistry) and Appelo & Postma (2007; Geochemistry, groundwater and pollution).
Hence the equations on lines 7 and 10 are – in our view – not the most recently used ones.

8. Same page; Ln. 11: Shouldn’t this be C rather than J in (1.6021 x 10^-19J)? Please explain. Same line, you forgot to add mol^-1 to 6.023x10^23 I think?

9. Same page, Ln. 21. We were unable to find this equation in Patterson et al. (1984) whilst you cite it. Please explain.

10. Page 351; Ln. 9: dimensionless index reflecting the likelihood of spontaneous nucleation of calcite. . . . Most of these considerations are, to my knowledge, based on stoichiometric calcite whilst most natural calcites are “dirty” containing substantial amounts of Mg, Fe, Mn etc. I would be most interested if you could please comment on the impact of increasing amounts of Mg in the crystal lattice of calcite and its impact on SNI? I do also find that you deal with the, in the context of your paper VERY important, principle of SNI in a rather brief manner. How about giving this some more space and explaining this a bit better to the non-specialist reader?

11. Same page, Ln. 25. I cannot encourage you to use the complex label “entropy” as a synonym for SNI and the equally complex label “enthalpy” for a synonym of T. I had many debates with my colleagues in geophysics and none seems to be able to agree on a proper definition of these terms. Why adding another level of complexity? Why not using temperature as such and SNI as such?

12. Page 353; ln. 5. I do like your list of different case examples; I find this the best part of your paper. I suggest that you provide a brief list of all case examples that you use in your study not only one per “system”. You also confuse me with Gibbs free energy here. This might be my mistake but do you refer to SNI here or something else? Did you properly explain what the relation between SNI and Gibbs free energy is? If so, please apologize but please realize that the reader is a bit lost here.

13. Page 358; Ln. 12: I guess this should be reference to figure 8 not to 8a, there is
no 8a in the figures I have with this paper.

14. Page 359; Ln. 1. I am particularly unhappy with the way you deal with the “oncoids” here. Why are they “superficial”. Also your illustrations in Figure 9 are below any resolution I can read. Neither in 9a nor in 9b I do recognize “oncoid”-like morphologies. Moreover, why should oncoids be oblate shaped? I am lost, sorry.

15. Page 361; Ln. 17: Here you refer to 490mgL-1 and to table 3. I am sorry, I failed to find this value in Table 3. Please explain. Same accounts for values in Ln. 18 and 19?? Along similar lines, Ln. 21. Here you refer to a pH of 7.5 – 8.3, these are not the values I find in Table 3. Along similar lines, I would politely disagree with you that Mg concentrations in Table 3 are similar! 1.3 mgL-1 is VERY different from 5.7 mgL-1. More, what is the significance of the decimals for Ca and Mg? I guess one decimal would do the job? More, why do you refer to Cell count per ml in table 3 and to cells L-1 on page 362; Ln. 6 etc. Frankly speaking, table 3 is a mess. Please clean up!

16. Page 373; Tab. 2. Some questions: Why would you not give us units? I assume T is in degree Celsius but what are the others? Is the Greek Phi Symbol between SD and SD denoting SNI? If so, why do you refer to use the small Greek letter Psi (as opposed to Phi) in Fig. 3 for SNI and none in Fig. 2? What you do here is the following: In the same paper, you refer to one parameter, SNI, either as the Greek symbol Phi, the Greek symbol Psi, the label Psi (Fig. 3), SNI and entropy? Is this a good idea? What is the difference between SD and SD? What is the meaning of the decimals for all these values?

17. Page 376; Fig. 2. Figure caption. I am lost, why is this an exponential scale? Similarly, Fig. 1. Why are these exponential scales, aren’t these log scales?

18. Page 377; Fig. 3. I am a bit confused looking at these data. For example, in the text, you separate several Italian depositional “systems” but here you seem to merge them again. Please explain. In the small inset to the upper right, you use T vs. Psi whilst you used SNI. So do you refer to the Greek letter Psi? If so, why would you use
a Greek letter and an English “translation” of a unit in the same figure. I guess this is really confusing readers. Finally, you seem to use the same symbol for Ddol and Plitvice?

19. Page 378; Fig. 4. In your figure captions you refer to figures 4D and E whilst I lack to see these figures in the figures in the version of the paper I have.

20. Page 381; Fig. 7. Stromatolite microherm. . . This terminology is controversial, pay attention.

21. Page 382; Fig. 8. What is the meaning of the white rectangle in the upper left corner?

22. Page 385; Fig. 11. I cannot read scales nor labels C and D. Please clean up.

Concluding, this paper has fundamentally an intelligent approach. I do like the idea and I would like to see the ms published. It seems that I am stuck with many moderate to small issues particularly with respect to the equations used. This might be in part my ignorance but it tells the authors, that this part needs attention. In any case, these problems leave the reader with many questions and I find the terminology used confusing (and in part wrong or so I think) in places. The quality of the tables and figures is substandard; I am disappointed that this version has gone to review.

I hope these comments are of use.

Adrian Immenhauser

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