

Interactive
Comment

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 Dr Rogerson,

As you will be aware we have now received two reviews on your manuscript “Linking process and product in terrestrial carbonates using a solution thermodynamic approach” that are both accessible as part of the interactive discussion. Both reviewers offer constructive criticism of the text and the methods utilised, but the reviewers also highlight some very significant deficiencies. In particular Adrian Immenhauser has provided a very detailed review of the methods section. Whilst both reviewers are broadly positive there appear to be inaccuracies in the equations used, as well as some misconceptions/tipos of the thermodynamic relationships as well as not using the most up to date equations. The difficulty is that these relationships have been used throughout

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the second half of the manuscript, potentially invalidating the entire approach.

I note some of the most serious issues below that echo some of the comments from A. Immenhauser. However, whilst there are parts of the manuscript that appear to be flawed in the current version, both reviewers express support for the general concept of the manuscript but there are many issues that will need to be addressed before this manuscript can be considered suitable for publication in ESURF. A particular issue to be certain of is that by correcting the thermodynamic approach, that your conclusions are not invalidated. In addition, the manuscript will need to be streamlined such that the non-specialist reader can follow the key points of the manuscript with clarity.

1 Major issues with the thermodynamic framework

pp 349: Ln 3, eqn. 1: I cannot understand this equation and cannot find it in Dandurand nor understand it conceptually. There seem to be some misconceptions here as usually one refers to the change in Gibbs free energy ΔG associated with a reaction or, hence I do not understand what is meant by the Gibbs free energy of an ion pair in solution. Does a solution does have a Gibbs free energy? Also it is not clear to me that a "carbonate solution" has a saturation state, as a saturation state is always with respect to a mineral. The problem with these apparent misconceptions about ΔG is that it is carried forward throughout the entire manuscript with the Gibbs free energy being discussed in each of the case studies but I believe this to be incorrect. In the cited Dandurand, 1982 reference (and indeed in any other reference that I am aware of), reference is always made to an excess of free energy, that is always associated with a chemical reaction such as CO₂ degassing.

pp349: Ln 20, eqn. 2: I believe this equation is also incorrect and echo point 5 of A. Immenhauser. Concentrations should be cited in moles/l and not just moles. Should K_{sp} not be the activity product? Regardless in what follows the equations used to

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estimate the activity equations can be at best regarded as antiquated and need to be updated to match recent research. Although correct to point out the limitations of some models/thermodynamic databases at high ionic strength, PHRQPITZ, designed for incorporating Pitzer's equations for calculation of geochemical reactions in brines are included in recent versions of PHREEQC and perhaps might offer a more up to date alternative. In any case how many systems do you have with $\text{pH} > 10$?

pp 351: SNI. In addition to the comments from A. Immenhauser, it is not at all clear to the reader how useful this is. For example, is this referring to either homogeneous or heterogenous nucleation? Presumably when applied to flowing waters the nucleation is always seeded to a large extent? There is again confusion here with the discussion of entropy and enthalpy, but most importantly there doesn't appear to be an adequate definition of SNI at all. At present I cannot recommend the use of the SNI at all, because it is not clear what it brings to the manuscript. I think I have followed the gist of the argument that the ΔG provided by degassing should not be sufficient to overcome the nucleation energy barrier, but this would need a much fuller treatment, considering composition, and considering seeded or heterogenous nucleation as alternative ways of reducing the nucleation energy barrier. I would also advise that entropy and enthalpy are not used in this context, as it is excessively complex and lends itself to confusion.

2 Other significant issues

Below are some of the more significant other issues.

2.1 Introduction

I can't help but think that the introduction would benefit from being broader. Terrestrial carbonates represent a significant reservoir of carbon, and perhaps this might provide

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a way in for the non specialist reader. There is a reasonable literature on this. Surely what really matters here is whether sedimentological or petrological processes might mask or blur any potential climatic signals. I think this is what is meant to be stated between lines 10-15, but the language needs to be tightened up. In fact surely this is the most novel point of the entire manuscript, to generate a process-based conceptual framework for the classification *and* understanding of terrestrial carbonates.

pp340, L28: The use of "journey" in this context is a little colloquial.

2.2 Figures and tables

There are numerous (too numerous) issues with the tables and figures. In tables the number of significant figures needs to be appropriate to the uncertainty, and units need to be provided. What does ϕ represent?

Figure 1: The scales are logarythmic and presumably "M" should be Mol/l?

Figure 3: Why in the legend state T vs Psi for each entry?

Figure 4: Figures D and E are missing

2.3 Other issues

- pp343, L27: Are you sure you mean desorption here?
- pp347, L12: cat ion = cation
- pp347, L17: physic-chemical = physico-chemical?
- pp352, L25: Not clear what is meant by non-tectonic in this context or why this is mentioned at all.

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3 Summary

I do hope that both the reviewer and my own comments will be of use in taking this manuscript forward. This is a complex area, and the manuscript tries to address many different issues. However, the content must be correct before this can be published.

Edward Tipper 24 October 2013

Interactive comment on Earth Surf. Dynam. Discuss., 1, 337, 2013.

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1, C227–C231, 2013

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