Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields

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Replies to Reviewer #1

We appreciate all efforts invested by the Reviewer in our manuscript and are grateful for the opportunity to resubmit a revised draft for your consideration. We address all comments from the Reviewer in the following itemized list, which we arrange enclosing each answer within corresponding review items. Please, note that Reviewer's comments and our responses are given in black italic and blue fonts, respectively.

Sincerely,

Yaniv Edery, Martin Stolar, Giovanni Porta, Alberto Guadagnini

Reviewer #1

The paper addresses a very timely and relevant topic in reactive transport through heterogeneous porous media. The most significant and novel result concerns the significant changes in non-Fickian transport behaviors while the while velocity variance display modest variations.

We thank the Reviewer for their careful review and positive comments.

The topic is suitable for HESS and I recommend minor revisions related to:
- The chemical model is a very simplified description of dissolution/precipitation processes. It should be better justified through additional references (see references below) and some quantitative information should be provided to describe its field of application. Without this information, the paper may appear like discussion around numerical experiments. Furthermore, the 'strange' dimension of the domain (60×24 cm^2) seems related to a lab. scale experiment….

While simplified, the chemical set-up follows previous work by Edery et al. (2011), where there is an extensive assessment of the employed formulation. This analysis is summarized in the supplementary material in this study, and will be further expanded following the Reviewer's advice.

The Reviewer is right. In line with the above mentioned work, our study is representative of a laboratory scale analysis. Yet, the precise dimensions have no particular implication and they are only selected to ensure a meaningful description of the correlation structure is included in the initial conductivity field. This will be duly clarified in the revised manuscript.

References
Y. Edery, H. Scher and B. Berkowitz, Water Resources Research **47** (8) (2011).

- A key parameter in dissolution/precipitation is the surface at the interface between solid and fluid, which is insufficiently discussed in the paper. Porosity and hydraulic conductivity are modified by precipitation/dissolution. What about the area in contact with the fluid?

We agree with the Reviewer that surface area is a key parameter when a kinetic precipitation-dissolution model is considered. Here, we consider local equilibrium. The precipitation and dissolution terms directly descend from algebraic calculations related to the local fluid equilibrium and are therefore not related to surface area. Note that this choice is functional to the specific objective of this work which is related to the characterization of transport under dynamic evolution rather than a detailed characterization of the reactive process and its effect on the pore-scale structure. This discussion will be included in the revised manuscript.

- 20 random realizations is a limited number of realizations… Can you discuss this number a posteriori, i.e. by analyzing the variability within realizations?

We have analyzed convergence of the results with respect to the number of realizations. As an example of the type of results we obtain, Figure R1.1 depicts the average of the temporal evolution of the sum of all conductivity changes |ΔK| in the domain as a function of the number of realizations considered for the most heterogeneous setting (values of conductivity changes being evaluated across temporal windows of width equal to 1 minute, as in Figure 4b in the manuscript). These results show that the number of realizations we employ is sufficient to characterize the reactive process, as quantified through the metric depicted. Results of similar quality are obtained also for the remaining values of initial log-conductivity variance examined.

While we think including Figure R1.1 in the revised manuscript will not bring additional value to the study, we will explicitly refer to such a preliminary analysis in our revised text.
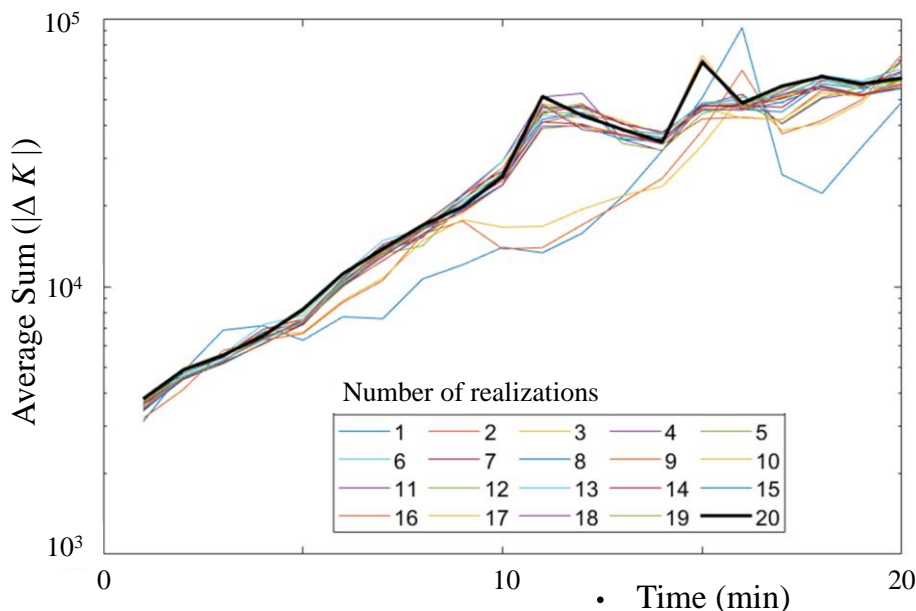
Figure R1.1. Temporal evolution of the sum of all conductivity changes |ΔK| averaged according to an increasing number of Monte Carlo realizations for the setting associated with initial log-conductivity variance $\sigma_0^2 = 5$. Values of conductivity changes are evaluated across temporal windows of width equal to 1 minute, as in Figure 4b in the manuscript.

- The particles are injected at regular time interval. Do they all start at the same time or is the injection time uniformly distributed over the time step?

  Particles are injected at the very beginning of each time step (each time step is of 6 s). This detail is now included in the revised manuscript.

- I do not understand why there is the number 3 in formula line 153.

  We fixed the typo and we thank the Reviewer for alerting us.

- I assume that the 20 minutes are for the initial pore volume (L234) ?

  Indeed, the Reviewer is correct and this is clarified in the revised manuscript.

References:
Lichtner, The quasi-stationary state approximation to coupled mass transport and fluid-rock interaction in a porous medium, GCA, 1988.
Dreybrodt et al., The kinetics of the reaction $CO_2 + H_2O + H^+ + HCO_3^-$, as one of the rate limiting steps for the dissolution of calcite in the system …, GCA, 1996.

  We thank the Reviewer and included these references in our revised manuscript.