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Discussions

Interactive comment on "Probabilistic assessment of field-scale CO_2 generation by Carbonate/Clay Reactions in sedimentary basins" *by* Giulia Ceriotti et al.

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Interactive comment on "Probabilistic assessment of field-scale CO2 generation by Carbonate/Clay Reactions in sedimentary basins" by Giulia Ceriotti et al.

Dear Reviewer:

We appreciate the efforts you have invested in reviewing our manuscript. We are now providing our responses to the comments received for your

consideration. In the following reviewer comments are in italic, our responses are in plain text, proposed changes in blue.

Sincerely,

Giulia Ceriotti (on behalf of all the authors)

This manuscript provides a three-dimensional test case study to assess the generation of CO2 by carbonate/clay reactions in a statistical framework. The authors extend the work of Ceriotti et al (2017) to a synthetic field setting. The article provides nice insights about the generation and source location of CO2.

We thank the Reviewer for the constructive review and comments.

I think that the article deserves publication after some minor corrections that should address several points:

(1) the authors should take some time to explain the source of uncertainty in equilibrium constants. Explain why the coefficients associated with equilibrium constants are random and which is the underlying process. Also, it is important to discuss the parameters describing this uncertainty from a realistic point of view. Are these values realistic? Do they compare with a real field?

We have revised the text to provide more context to our choices and with reference to the main elements associated with modeling and propagation of uncertainty. As mentioned also in our response to Reviewers 1 and 2, we consider uncertainty associated with equilibrium thermodynamic constants because our application requires to extrapolate these beyond the temperature and pressure conditions at which they are typically evaluated. The probability distribution functions associated with these uncertain parameters are taken from our previous work Ceriotti et al. (2017). We have now amended the Supplementary Material and provided more details about these aspects.

It is not clear why the authors state that equilibrium constant Ks,ph depends on pressure and temperature but equation (1) only has temperature and is valid only for p=1 bar;

The effect of pressure is taken into account by Equation (3), following classical approaches in equilibrium geochemistry.

(2) some of the assumptions are not clear but from the introduction I was expecting some two-phase flow simulations besides generation;

We have revised the Abstract and Introduction to sharpen the description of the objectives of our work and avoid misunderstandings. The objectives are now stated as follows in the Introduction:

"Modeling of CO2 generation and accumulation in large-scale geological systems is typically prone to considerable uncertainties, chiefly due to paucity of information and to the large spatial and temporal scales involved. In this context, we provide a modeling framework that leads to a probabilistic quantification of the generation of CO2 by a specific class of reactive processes (i.e., CCRs). As such, our study fills a knowledge gap by providing a methodology to support quantitative investigations of spontaneous CO2 generation in large scale geological systems, these being otherwise typically based on mostly qualitative analyses. While we consider a simple geochemical model based on thermodynamic equilibrium, our probabilistic framework of analysis is flexible and can include treatment of model uncertainty (Walker, 2003; Neuman, 2003) as an additional element. Setting a given model structure is simply a convenient choice to minimize computational and conceptual complexity while at the same time considering a mathematical model that can be characterized with information that is typically available in field scale settings (in terms of, e.g., mineral composition, pressure, and temperature distributions). Values of equilibrium constants are here considered as uncertain because temperature and

pressure values observed in sedimentary systems lie outside the range of conditions where these parameters are usually characterized (Ceriotti et al., 2017; Blanc, 2012). In this work we investigate the propagation of this parametric uncertainty in the presence of various (alternative) CCR formulations by focusing on a three-dimensional scenario. When considering the framework proposed by Walker et al. (2003), our work allows combining uncertainty in model parameters (equilibrium thermodynamic constants) with input uncertainty, i.e., uncertainty in the description of the reference system. The latter type of uncertainty is reflected by our choice of considering diverse mineral assemblages leading to the occurrence of different CCRs. Note that our approach is geared towards quantification on the space-time location and intensity of the CO2 source. This information can then be used as input to quantify scenario uncertainties, by delineating the spatial and temporal extent of CO2 influx. Transport and accumulation of CO2 across the subsurface can then be analyzed through approaches such as those described, e.g., in Battistelli et al. (2016). From an operational standpoint, our approach could be applied to enhance our knowledge on the degree of compatibility of CO2 concentrations observed in field scale systems with the occurrence of CCR, as opposed to the action of other processes which might be considered in a large scale transport model of choice. The study is structured as follows (. . .)"

(3) the authors state too many times that something can be found in Ceriotti et al (2017), this makes the description of methods not self-contained;

Prompted by the Reviewer's concern, we have provided more context to the methodology in the Supplementary Material. Here, we include an outlined description of the procedure used to derive the statistics of the uncertain thermodynamic parameters starting from raw data included in Blanc et al. (2012).

(4) not clear what do you mean by phases in equation (2) and reaction CCR, may be this is too abstract, and the authors should give an example to follow;

We replace the wording “phase” with the more explicit “mineral phases” when needed in Sections 3 and 4.

(5) sorry if I miss this one but I do not see the definition of C_A, not clear how is it calculated.

C_A is the frequency of activation of a CCR at a given spatial location (x, y, z). We have rephrased its definition at line 260.

Other than this, I think that the manuscript is well written and organized and will be a nice contribution for HESS. I did not see typos except in line 162 where you are missing “it is”.

Thank you, we fixed the typo.

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