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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)

The manuscript provides a showcase for a probabilistic framework at hand of a realistic 3D scenario. The processes under investigation generate CO2 from complex Carbonate/Clay Reactions in deep sedimentary basins where pressures are high and temperatures play a role in fundamental reactive systems. In the following and in the manuscript, these systems are denoted as CCR. As I understand the motivation for this study, it extends previous work of a lower-dimensional concept into full 3D and may be seen as a proof of concept. We have here a manuscript that falls within the scope of HESS, presents a novel concept with well explained scientific methods. The title is not wrong, but maybe promises too much. It is rather a proof of concept for a probabilistic framework, with still a way to go for an 'assessment'. So, I can support this study for publication in HESS, while I have some major concerns, which I am confident can be addressed.

We thank the Reviewer for their analysis of our work. We understand that the wording "assessment" in the title might have caused some misunderstanding on the key objective of our study. Thus, in our revisions we have taken also this element into account and have revised the manuscript Title and Abstract to sharpen the focus of our study.

Title is modified as follows:

"Probabilistic modeling of field-scale CO2 generation by Carbonate/Clay Reactions in sedimentary basins".

Accordingly, we rephrase the Abstract at lines 1-2 as follows
"Abstract. This work explores a probabilistic modeling workflow and its implementation targeting CO2 generation rate and CO2 source location by occurrence of Carbonate/Clay Reactions (CCRs) in three-dimensional realistic sedimentary basins. We ground our study on the [. . .]".

To avoid any misunderstanding, we recast some sentences in Sections 4 and 5 as follows:

- At line 247 "We tackle probabilistic modeling of the CCRs introduced in Section 1 upon relying on a numerical Monte Carlo (MC) approach".
- At line 300 "According to our probabilistic modeling framework, the distribution of [. . .]".
- At line 326 "Our probabilistic model documents that the characteristic temperature and pressure [. . .]".
- At line 384 "We rely on a probabilistic modeling framework to model CO2 generation [. . .]".

General comments:
I) The research question(s) that guide(s) this work should be formulated more clearly, and be addressed more clearly. I see here two fields where new knowledge is produced, (i) about the probabilistic framework itself, its concept, limitations, applicability, (ii) new insights on CCR and their role in generating CO2 in sedimentary basins (e.g. the statement in Line 295/296 on pressure playing a major role in CCR activation though having minor impact on reaction equilibria). Accordingly, the structure of the

manuscript, and in particular the discussion and conclusions should reflect this: in the introduction, in the results, and in the conclusions. On the physics part, I took home messages like, e.g., pressure matters to build a gas phase, temperature affects equilibrium constants, thus burial depth; or: one CCR is less likely activated while it produces more CO2 than another one. And regarding the probabilistic framework, I am actually not sure what I learned here, see my next point.

We consider uncertain equilibrium thermodynamic constants because sedimentary settings require considering temperature and pressure conditions lying outside the ranges where these parameters are usually appraised. A similar choice was illustrated in one of our previous studies (Ceriotti et al., 2017). Here, we show how considering this source of parametric uncertainty propagates to key outputs when a three-dimensional scenario and alternative mechanisms are considered, thus incorporating an additional source of uncertainty. Note that considering a three-dimensional case is relevant because it allows obtaining a space-resolved delineation of the identified CO2 sources and a quantification of the related fluxes.
While we prefer not to change significantly the structure of the manuscript, we have revised the Introduction and our Conclusions to pinpoint the key elements of innovation associated with the probabilistic framework illustrated in this work.

The revised Introduction now reads (starting from line 93 of the original manuscript):
"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 (. . .)"

Conclusions, line 385 is modified as follows:

"Our work is grounded on the probabilistic approach proposed by Ceriotti et al. (2017) to treat Carbonate/Clay Reactions (CCR). Such an approach embeds quantification of parametric uncertainty associated with the thermodynamic equilibrium constants

driving CCR and has been showcased by these authors in a one-dimensional set-up".

Conclusions item 1 is modified as follows:

"We rely on geochemical equilibrium and quantify uncertainty associated with model parameters and inputs, the latter source of uncertainty corresponding to the uncertainty in the information required to describe the reference system (i.e., input uncertainty; Walker et al., 2003). The presence of input uncertainties implies the possibility that diverse CCRs may occur and lead to differing degrees of importance of parametric uncertainty on CO2 generation. Our stochastic framework (. . .)"

Conclusions item 2 is modified as follows: "We quantify the way the considered input and parametric uncertainty propagates onto estimates of generated mass of CO2 in a three-dimensional system. This allows describing the extent and the shape of the CO2 generating source together with the associated CO2 generation rate. (. . .)"

II)The probabilistic framework includes some uncertainties (on equilibrium constants) while it takes strong assumptions in many instances. This is acknowledged in the last remarks in the Concluions section. In fact, the list of uncertainties is endless. Understanding even more extended probabilistic frameworks becomes even more difficult, and I fear results get lost in a smoke bomb of probabilistic interpretations. That statement, of course, is exaggerated. But seriously, regarding the classification of uncertainties: first of all, I found it not easy to understand from Abstract and Introduction what the motivation for the "probabilistic assessment" is, i.e. where are the uncertainties. Examples might be given in the Introduction. Otherwise, it takes until Section 3 to find it out. Or in Lines 139-141: my impression is that deciding the mineralogical compositions are uniformly distributed is a strongly simplifying assumption, although anything else would only increase complexity, not reliability in any sense. But does this not reduce the informative value of the overall framework, when such crucial statistical uncertainties are neglected. Therefore: It might be helpful to put the probabilistic framework into a broader context of a clear classification of uncertainties occurring in the application of the framework. E.g. Walker et al. (2003) use definitions of differ-

ent categories, like determinism, statistical uncertainty, scenario uncertainty, etc. This might help keeping an overview and in interpreting the results.

We thank the Reviewer for this comment which prompts us to improve the way the key objectives of the study are framed. We also elaborate further on our choice to consider a spatial uniform mineral assemblage.

These points are now addressed in Section 3. The introductory paragraph of this Section now reads (line 154 of the original draft):
"Our study relies on a given model structure, thus neglecting uncertainty in the latter. We rest on the equilibrium-based approach used by Ceriotti et al. (2017). Thus, we consider pure mineral phases while neglecting other factors which would eventually influence the model structure (e.g., the occurrence of other mineral transformations, or effects associated with salinity of brine). Consistent with this model structure, we consider the equilibrium constant of speciation reactions as the key source of parametric uncertainty. We note that this choice is motivated by the observation that temperature and pressure values observed in sedimentary systems lie outside the range of conditions where thermodynamic equilibrium constants are usually characterized (Blanc, 2012). In addition to parametric uncertainty, we also consider input uncertainty, defined as the uncertainty related to the description of the system (Walker, 2003), i.e., we assume that diverse CCRs may take place depending on the mineralogical assemblage. These two sources of uncertainty are propagated throughout the final modeling goals of interest, i.e., the CO2 source location, the CO2 generation rate, and the temperature and pressure of CCR activation. Note that, as detailed in Section 2, we consider a uniform mineral composition across the domain, a setting corresponding to an upper limit condition for each of the considered CCRs. While it would be interesting in principle to investigate the impact of a spatially heterogeneous mineralogic composition, doing so would require having at our disposal on a suitable dataset and would increase complexity. Yet, it is worth emphasizing that the proposed methodological framework and modeling approach are fully compatible with the presence of a spatially

variable mineralogical composition, which can be accommodated in the presence of appropriate data to characterize it. As such, our approach can be employed to assess the impact of uncertainties associated with spatially heterogeneous arrangements of mineral and sediment composition on CCR-based CO2 generation. The latter could be tackled upon relying on appropriate techniques such as, e.g., Functional Compositional Kriging (see, e.g., Menafoglio et al., 2016, and references therein). Analyzing this aspect is, however, beyond the scope of the present study."

Specific comments:
1) Line 154-155: How should I understand the statement that the equilibrium constant of speciation reactions is the key source of uncertainty? Does this mean a bigger uncertainty than spatial distribution/heterogeneity and choice of CCR? Probably not.

We are confident that the motivation at the basis of our choice is now clearly stated and has been addressed through the revisions outlined above.
2) Line 213-214: Compatible sounds not wrong and I think, it is absolutely correct to use this wording. The data do not disagree with the model, but what is the message in concluding that the model does not contradict observations? Compatible sounds so weak that it demands for more explanation and interpretation. I am also not sure, but maybe the authors have an idea.

In our opinion "compatible" is an appropriate expression. Identifying the source of CO2 accumulations for each of the listed basins is beyond our scope. Modeling can refine and enhance our understanding of the effects of alternative processes that may contribute (jointly or exclusively) to CO2 accumulations. However, only after a dedicated analysis of a specific study it would be possible to formulate hypotheses on the relevance of CCR in a real case also in comparison with other processes (e.g., magma degassing, biologically driven processes or other geochemical/geological processes). For this reason, we would prefer maintaining the wording compatible in the revised manuscript.
3) Conclusions: Am I right to assume that you suggest for a beneficial application of

this framework, the CCR should be known in advance?

When detailed information / observation on mineral compositions are available, one or more CCRs can be identified as possible CO2 sources. Our framework enables one to jointly consider alternative CCRs when such information is not available, thus fully embedding the effects of such uncertainty in the desired modeling goals. This is clarified in the revised manuscript Conclusions starting from line 397.
"[. . .] Our stochastic framework allows quantifying the (spatially- and temporally-dependent) probability distribution of the activation temperature and pressure associated
4) Conclusions, Lines 411ff: I do not really get the message of this statement. What exactly does 'physically-based modeling' refer to?

Our revised text now reads: "(. . .) provides a proof-of-concept of the applicability of process-based probabilistic frameworks for quantitative modeling of CO2 accumulation in subsurface systems".

Minor comments, typos, etc.:
a) Abstract, Line 3: I was wondering if 'mono-dimensional' is a known expression. If so, I am Ok.

We changed it to one-dimensional.
b) Line 25: 'relatively'
c) Lines 92, 210, and 212: 'formulations'
d) Line 162: it IS always possible
e) Line 312: is depicted (blank missing)
f) Line 401: 'values'

These typos are now fixed.

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