Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2020-525-AC2, 2021

Hydrology and Earth System Sciences
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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Received and published: 14 March 2021

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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 paper outlines a probabilistic framework to assess the evolution of CO2 in a “realistic” 3-D deep sedimentary basin. It builds on a relatively recent study (in GCA) also led first author G. Ceriotti that explored a method to quantify the impact of one type of carbonate/clay reaction (CCR) in a 1-D basin scenario. In this follow-on study they expand their assessment to include other types of CCFR. The overarching goal of this new study is to interrogate, in 3-D, the distribution of CO2 generated by the CCRs in a temperature-pressure regime dictated by the boundary conditions of their basin model system.
Scientific significance: Does the manuscript represent a substantial contribution to scientific progress within the scope of Hydrology and Earth System Sciences (substantial new concepts, ideas, methods, or data)?
Understanding the behavior of C-O-H fluids in sedimentary basins is certainly a timely topic especially with the recent emphasis on the extraction of gas and oil from tight formations and the potential for storage of CO2 in the subsurface to mitigate anthropogenic greenhouse gas emissions. This paper tackles this problem by defining a 3-D basin burial scenario dominated mainly by dolomitic rock units with overlying shale caprock. They refer to a widely tested and documented burial model known as ESIMBA which admittedly I have not heard of before (TOUGH, TOUGH2, iTOUGH and TOUGHREACT are examples of codes familiar to this reviewer). If their burial model tied to a probabilistic

approach tracks fluid evolution via the carbonate-centric reactions they identify while at the same time documenting the evolution of porosity and permeability leading to the CO2 distributions they identify, then perhaps yes this may be a nice contribution to the understanding of basin processes. However, based on what has been presented, I found it somewhat difficult to assess how their outcomes connected these coupled processes. I would like to have seen how porosity and permeability evolve during the burial process and how in turn these are related to the true distribution of CO2. Their visualizations illustrate where CO2 is enriched but they seem to cover a wide region of certain horizons. I guess this just means there is a high probably of finding a specific FCO2 value in this area. Rating: Good

The codes referenced by the Reviewer are excellent examples of reactive transport computational tools aimed at modeling flow, transport, and reactive processes in subsurface environments. Burial models, such as ESIMBA used in this work, are developed to simulate geological processes governing the evolution of deep subsurface environments involving extremely slow phenomena (whose reaction rate is hard to evaluate) developing across considerably large spatial and temporal scale, such as, e.g., diagenetic processes. Evolution of porosity along with the diagenetic process is included in the model ESIMBA, as explicitly stated at line 115 in the original version of the manuscript. We did not include a figure portraying a three-dimensional spatial representation of porosity distribution (of the kind, e.g., similar to what has been done for temperature and pressure in Figure 3) because porosity variations have only a mild influence on the outputs of our study. We then point out that our approach allows characterizing CO2 sources and may be then coupled with reactive transport models such as those mentioned by the Reviewer (see also Battistelli et al., 2016). We emphasize that modeling of CO2 migration and the ensuing dynamics is beyond the scope of our study, which targets a quantitative probabilistic characterization of space-time location and intensity (quantified as source or influx, FCO2) of CO2 sources. To avoid ambiguities (for which we apologize), this is now explicitly stated in the following revised paragraph in the Introduction:

"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.".

Scientific quality: Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way (consideration of related work, including appropriate references)?

The application of probabilistic methods with associated statistical underpinning and Monte Carlo simulation is certainly one way to assess geochemical processes in an evolving sedimentary basin. The goal is to track the three reaction types in space and time as the basin evolves. The frequency of CCR and associated distribution of the resulting CO2 reaction product are visually represented in 3-D very clearly (Fig. 7-9). I am very appreciative of their attempt to constrain the different levels of uncertainty but must admit I found their narrative describing uncertainly somewhat unwieldy and difficult to follow. Further this made it hard for me to understand how these uncertainties influenced the kinds of outcomes they represented on the key Figures 6 – 9.

We thank the Reviewer for appreciating the approach and the figures that we have proposed.

We do hope that the revised manuscript can facilitate appraising the main focus of our study, which is keyed to the formulation of a flexible stochastic modeling framework capable of embedding diverse sources of uncertainties in the target environmentally relevant scenario. This is now further elaborated in Section 3, where we add the following revised text:
"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."

Perhaps it is not fair to criticize the nature of how they defined their sedimentary system, but I do have to wonder about the justification for selecting a dolomitic-rich rock as one of the starting lithologies. Dolostones are certainly not uncommon in the sedimentary record, reportedly making up to 2 percent of crustal rocks. However, a large percentage of the dolomite in thick marine dolostone units is thought by many geologists and geochemists to have been formed by replacement of CaCO3 sediment rather than by direct precipitation. This authigenic process can start near the surface but is certainly facilitated by deeper burial involving the evolution and transport of Mg-rich brines infiltrating the calcite-rich formation; this reaction can yield a pretty big increase in porosity up to 14%. So, to me a more "realistic" basin scenario would be to start with a limestone, alter it to dolomite during burial with the associated porosity (and permeability) change, and then with deeper burial initiate the alteration reactions of the sort they identify.

We thank the Reviewer for pointing out an alternative interesting scenario of sedimentary basin evolution. The probabilistic approach presented in this work is fully compatible with the sedimentary basin scenario suggested by the Reviewer. The latter setting can be included in our workflow by replacing the spatially homogeneous mineralogy scenario considered in the manuscript with a scenario according to which mineralogy varies with the temporal progressing of the burial process, eventually capturing the transformation of calcite into dolomite.

We clarify that the terminology realistic we use referring to the basin considered is linked to its geometry and pressure and temperature ranges and distribution. As stated in the original manuscript (lines 136-138), the mineralogical assemblage is selected to maximize the generation of CO2 based on the stoichiometric balance of the CCRs analyzed. The purpose of presenting such simple mineralogical composition is to focus on (a) demonstrating the applicability of the proposed probabilistic workflow to three-dimensional systems and (b) illustrating how to analyze and interpret the richness of information that can be obtained employing such a methodology when investigating a case study of interest given a selected mineralogical assemblage.

I also appreciate the impetus for picking specific simple mineral assemblages as a starting point for the modeling, but beidellite is not a phase typically observed in deep shale systems. And I have yet come across a shale (mudstone) with 42% microcline; this level of feldspar plus 50% clay would make this a very unusual rock.

We thank the Reviewer and highlight that the methodology presented in not linked to the specific mineral assemblages or CCRs considered in this work. The choice of including a suite of three CCRs and different mineral assemblages (which maximize the generation of CO2) is aimed at showing that our probabilistic workflow is flexible and can be readily adapted to include any mineral assemblage and CCR of interest. This is now clearly discussed in the revised Section 3.

There are few things I am concerned about with respect to the reactions they picked. These represent just a very small number of possible reactions that

could take place during burial. So why not define the starting mineralogy, initiate the burial process of increasing P and T, and let thermodynamics drive the water-rock interactions to the most favored stable reactions. A priori selection of the reactions seems rather narrow in thinking, although I do appreciate, they wanted to target the most optimum reactions to produce CO2 but is this truly "realistic".

We apologize if the use of the expression *realistic* in the original manuscript has generated some misunderstanding about the target of our work. Our intent was to indicate that the system we consider is subject to conditions associated with space-time history of pressure and temperature which is consistent with what one can observe in a sedimentary basin and characterize through a burial model. We clarify this point in the revised manuscript (particularly, Abstract, Introduction, and Section 2) by specifying that the expression realistic sedimentary basin is employed to denote the three-dimensional evolution and distribution of environmental pressure and temperature. We agree with the observation of the Reviewer about the variety of possible reactions taking place in a complex geochemical setting of the kind associated with a sedimentary basin. However, we note that considering an increased complexity system of reactions (relying, e.g., on databases typically included in geochemical models) would require including also a larger collection of uncertain parameters, thus rendering the problem hardly tractable, at least at the current stage of development. In the context of uncertainty quantification associated with geochemical processes, a simplification of the underlying conceptual model is required, this being an appropriate choice as long as the simplified model is still able to capture the key traits of the evolution of the main target output variables of interest. We analyzed the consistency of the outputs of our simplified conceptual model with the results proposed by a widely used geochemical software (i.e. Phreeqc; Parkhurst and Appelo, 2013) under various conditions of pressure and temperature. For completeness, we illustrate in the following the results obtained for reaction CCR1 which can also be found in the Electronic Annexes of Ceriotti et al. (2017). We selected the temperature (T) and pressure (P) combinations observed in our sedimentary basin showcase listed in Table 1 together with depths at which these conditions are found. Note that this analysis is confined to temperature values below 300 °C, higher temperature values being outside the range of applicability of the Phreeqc software and Thermoddem database. The software Phreeqc is then used to simulate the geochemical system and evaluate aqueous and gaseous speciation when mineralogical phases associated with CCR1 are considered (see Figure 1 depicting the corresponding screenshot from the Phreeqc code).

Depth [m]	P [bar]	T [° C]
1421	197.00	99..00
1970	251.00	121.40
2504	303.00	141.00
3071	359.00	160.90
3661	416.80	180.30
4301	479.00	200.00
5004	548.50	222.00
5621	609.00	240.90
6310	679.40	261.00
6919	736.10	280.50

Table 1. Values of pressure (P) and temperature (T) resulting from the burial model at diverse depths at time t = 0 Ma.

Figure R.2 depicts (in logarithmic scale) the activities and molalities of these dissolved species as a function of depth. Results from Phreeqc are juxtaposed to the probability density function (denoted as $f_{C,Z}$) of CO2 fugacity resulting from our simplified model in the same conditions. We consider the results of

Figure_R_1.png

Fig. 1. Code implemented in Phreeqc to compute molalities and activities of the diverse aqueous species contributing to the molality/activity of dissolved $C(4)$ (i.e., $CO_{2(aq)}$; $HCO^{-}_{3(aq)}$; $Ca(HCO_3)^{+}_{(aq)}$; $CaCO_{3(aq)}$;CO_3^{2-}, and $MgCO_{3(aq)}$) for the values of temperature and pressure listed in Table 1.

our simplified geochemical system fully consistent with those obtained upon relying on the simulation of a complex network of reactions.

Figure_R_2.png

Fig. 2. Activities and molalities of the aqueous species contributing to the molality/activity of dissolved C(4) as computed through the Phreeqc software relying on the Thermoddem database compared to CO2 fugacity yielded by our probabilistic modeling.

Second, they consider a system where the fluid is pure water which is very unrealistic when is it comes to sedimentary basin fluids; most are saline (typically 50-100 g/kg TDS). This would change the activity of water and in turn impact the solubility of the CO2 (the salting-out effect). High concentrations of CO2 would also affect the activity water. And to be sure a different activity of water *would impact the nature of the reactions they did identify.*

As pointed out by the Reviewer, the ionic strength of the brine may have a marked impact on the geochemical behavior of CO2, as dissolved or gaseous phase.
As also acknowledged by the Reviewer, salinity of the brine may vary broadly in sedimentary basins. This issue should be approached in the context of a probabilistic assessment, in agreement with the main concept underlying our work.
Indeed, the selection of a certain level of salinity of the brine is an imposed initial condition, which can be as well subject to uncertainty due to our incomplete knowledge of the processes involved and other initial/boundary conditions in sedimentary environments. In this context, the choice of pure water is just one of the possible modeling scenarios. We agree that different (and perhaps more realistic) scenarios may be formulated, upon relying, e.g., on available information, which may be available from modeling or field observations on a specifically targeted sedimentary system. However, we remark that our study is focused on the quantification of parametric uncertainty and assumes a selected model structure which does not consider ionic strength. The motivation underlying our choice is now clarified in the revised Section 3, as reported in the following.
"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 val-

ues 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."]

Third, they seem to pull thermodynamic data from what I consider outdated references. For example, Ian Hutcheon's work is certainly respected, but the authors should be very careful using thermodynamic data/insights that date back over 20 years. I recommend the authors take a journey through some the sources provided here (and associated references) just to be sure they are on the right path (this falls into the category of capturing "thermodynamicuncertainty"): Modeling Metamorphic Rocks Using Equilibrium Thermodynamics and Internally Consistent Databases: Past Achievements, Problems and Perspectives Pierre Lanari, Erik Duesterhoeft Journal of Petrology, Volume 60, Issue 1, January 2019, p. 19-56 https://doi.org/10.1093/petrology/egy105 CHNOSZ: Thermodynamic Calculations and Diagrams for Geochemistry Jeffrey M. Dick Front. Earth Sci., 16 July 2019 https://doi.org/10.3389/feart.2019.00180 Thermodynamic Data for Geochemical Modeling of Carbonate Reactions Associated with CO2 Sequestration – Literature Review (only focuses on carbonates but still may be useful) KM Krupka KJ Cantrell BP McGrail: September 2010 Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830 Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems T. J.Wolery and C. Jove-Colon ANL-WIS-GS-000003 REV 00 November 2004 Zimmer, K., Zhang, Y.L., Lu, P., Chen, Y.Y., Zhang, G.R., Dalkilic, M. and Zhu, C. (2016) SUPCRTBL: A revised *and extended thermodynamic dataset and software package of SUPCRT92. Computer and Geosciences 90:97-111.doi.org/10.1016/j.cageo.2016.02.013. Rating: Good (leaning toward Fair)*

We thank the Reviewer for the constructive comment and for bringing these relevant references to our attention. While the works of Hutcheon are seminal in the context of CCR geochemistry, they do not constitute the source of the thermodynamic data used in our study. Thermodynamic data are taken form the Thermoddem database (Blanc et al., 2012) due to its completeness, traceability of data, and proven internal thermodynamic consistence, especially for the aluminum silicate phases (Blanc et al., 2015). We now detail all data sources in the manuscript by including the aforesaid literature references in Section 3.1 and in the Supplementary Material where thermodynamic data of all phases included in the work are listed in Table S1. Additional details on the procedure for estimating the uncertainties associated with thermodynamic constants starting from raw data are also included in the revised version of the manuscript (as Supplementary Material) to clarify the source of these information.

Presentation quality: Are the scientific results and conclusions presented in a clear, concise, and well-structured way (number and quality of figures/tables, appropriate use of English language)?
Given the approach they adopted, the results and conclusions seem reasonable. But that said, this does not make them necessarily significant or innovative. They took an interesting approach with their probabilistic modeling then seemed to engineer the outcome they wanted by orchestrating a narrow type of reaction chemistry rather than truly allowing a more realistic mineralogic system to evolve during burial. I appreciate the probabilistic approach differs significantly from say a full developed 3-D reactive transport model that allows the system to track the thermodynamically most favorable reactions with accom-

panying fluid evolution. And this of course only considers the system from an equilibrium thermodynamic point of view.
Although more difficult, one could also address the evolution of the model system by quantitively assessing where and when the system deviates from equilibrium during burial. I guess I was hoping for better articulation of the connection between the evolution of the mineralogy and CO2 and the changes in porosity-permeability. For example, was CO2-rich fluid allowed to migrate from one unit to another or was every rock unit treated as a closed system.
The probabilistic approach is certainly interesting but seems to fail in capturing the dynamics of a complex heterogenous system undergoing change over nontrivial length and time scales.
So, what did we learn from this paper? We learned that if you take a dolomite-bearing or dolomite-rich rock containing other phases like some clay or feldspar and push the rock to higher P and T approaching low-grade metamorphism in a deep basin you can make lots of CO2. I think we kind of already knew this. What would have been really interesting to see is how this CO2 concentration changed as burial proceeded for each rock unit as a function of space and time, and how these changes affected the porosity and permeability of each unit. I am thinking they may have such information and if so, I encourage them to expand their outcomes to be more inclusive.
Rating: Good
We agree with the Reviewer about the observation that our model does not include a high number of processes and is a streamlined representation of the geochemical burial complexity. Considering equilibrium rests on the hypothesis that the water-rock system located at a certain depth attains equilibrium before being buried to a deeper level. Thus, it is the burial velocity that limits the rate in the generation of CO2. This is indeed implicitly embedded in Equation (6) of the manuscript and fully acknowledge in Ceriotti et al. (2017). For complete-

ness and clarity, we now explicitly state this element in the revised manuscript when presenting Equation (6) (lines 230 - 245).
We further emphasize that our work is not aimed at a comprehensive description of all bio-geochemical, geological, and fluid dynamics processes taking place in a sedimentary basin during diagenesis. The scope of the study is to present and apply a methodological framework and workflow for the probabilistic quantification of CO2 generation sources. As mentioned above and in the response to Reviewer 1, we revised parts of the Abstract, Introduction, and Conclusions to unambiguously clarify this element and avoid misleading terminology which might lead to expectations of the formulation of a full biogeochemical and geological model.

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