Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2020-525-RC2, 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.

Anonymous Referee #2

Received and published: 19 January 2021

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 sci-

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entific 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 E-SIMBA 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

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

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Discussion paper

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. 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. 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. 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". Second, they consider a system where

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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. 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 "thermodynamic uncertainty"):

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)

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 accompanying 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 non-trivial 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

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have such information and if so, I encourage them to expand their outcomes to be more inclusive.

Rating: Good

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