Linking chemical weathering, evolution of preferential flow paths and transport self-organization in porous media using non-equilibrium thermodynamics

Evgeny Shavelzon[1], Erwin Zehe[2], and Yaniv Edery[1]

[1]Faculty of Civil and Environmental Engineering, Technion - Israeli Institute of Technology, Haifa, Israel
[2]Karlsruhe Institute of Technology (KIT), Institute of Water and River Basin Management, Karlsruhe, Germany

Correspondence: Yaniv Edery(yanivedery@technion.ac.il)

Authors' replies to Reviewers

This document contains replies to Reviewers' comments. We appreciate the time and effort invested by the respectable Reviewers in our manuscript and are grateful for the opportunity to resubmit a revised draft for your consideration. We address all Reviewers' comments in the following itemized list, arranged such that the answer to each review item is located directly below the item. Please note that Reviewers' comments and our responses are given in black and blue, respectively.

All proposed changes have been implemented in the updated manuscript. Due to suggested major revision, significant parts of the manuscript were rewritten or significantly updated. Therefore, in the attached Track changes document the changes are marked in blue. Sincerely, Evgeny Shavelzon, Erwin Zehe and Yaniv Edery.

Replies to Reviewer 1

Reviewer 1

- This manuscript is about the dissolution of calcite in porous media and the resulting self-organization of preferential flow paths. The results are based on numerical simulations and are analyzed with the help of thermodynamic variables. Although the basis of the model seems to be similar to what has been assumed in models of karst evolution for decades, I found this study very interesting. The are numerous points to think about. On the other hand, I find it a bit too difficult. Each step is not really difficult in itself, but in sum it is very challenging not to get lost. When reading it, I had to go back quite often to find out whether something is indeed not clear or whether I just missed it. So, I am a bit afraid that scientists who did not have to hold on to write a review will likely give up.

We thank the Reviewer for their careful review and positive comments that were extremely helpful in clarifying and improving the readability of the manuscript. Indeed, as the reviewer has pointed out, the main point of the study is the analysis of the process of geochemical weathering within thermodynamic framework and establishing the correlation between chemical weathering and the emergence of preferential flowpaths in the system, rather than the modeling of the geochemical process itself, which has been done previously. We are thankful to the reviewer for indicating the need to improve the readability of the manuscript, clarifying it and making it more concise. We fully acknowledge this need and are committed to amending the manuscript accordingly. Please find attached the summary of our suggestions regarding improving the readability towards the end of our reply.

– So let me just make some suggestions, hoping that they may be helpful for clarifying some aspects. Quite in the beginning, I wondered about the porosity and permeability (Eqs. 7 and 8). If I got it correctly, you assume constant initial permeability and introduce spatial variability be assuming a variable factor in the Kozeny-Carman relation. This looks unconventional. The conventional approach would be the same factor, but variable initial porosity. I guess that you used this approach in order to define the pore volume time. However, I think that it also has an effect on how the development of the permeability. In your approach, a given change in porosity (from the constant initial value) introduces the same relative change in permeability. In the more conventional approach, the relative change would be smaller for cells that already have a high permeability. So I would guess that the formation of preferential flow paths in stronger in your approach than in the conventional version. This makes we wonder whether it has an effect on the results. Maybe you can clarify this aspect.

We thank the reviewer for addressing this important point. The constant initial porosity assumption was introduced in order to facilitate the chemical aspects of our reactive transport model, namely the calculation of the molar amount of H^+ to give pH of 3.5 in a computational cell. This allows to estimate the current pH in the cell and, thus, the direction and the extent of reaction there (see Section 2.3 in Shavelzon and Edery (2024) for details). This assumption was deemed acceptable, as the purpose of our simplified chemical reaction setup is to capture the qualitative dynamics of the complex process of geochemical weathering, thus making it possible to simulate and analyze the complex reversible behavior using a relatively unsophisticated model.

In our model, the change in porosity of a specific cell in the computational field is determined by the amount of reaction that has occurred in a cell during the current time step, as dissolution/precipitation of calcite increases/reduces the void volume of the cell (as expressed by Eq.(9) in the *updated* manuscript). Given the initial and the updated values of porosity in the cell, as well as the initial permeability value, we are then able to calculate the updated permeability in the cell using the Kozeny-Carman relation as shown in Eq. (10) in the updated manuscript. Notice, that Eq. (10) includes both initial and updated porosity values in a nonlinear relation that cannot be expressed as a function of only a change in porosity. Therefore, the relative change in permeability does depend on the initial porosity value. To demonstrate

this, we attach below the plot of the Relative change in permeability as a function of porosity K_{k+1}/K_k, as given by the expression in Eq. (10) as a function of initial porosity θ_k, for the change in porosity $\Delta\theta = 0.05$ - see Figure 1 in the current document. We observe that for larger θ_k values, that correspond to higher permeability, the relative change in permeability is smaller, just as is physically expected. In our model, we make a simplifying assumption of constant

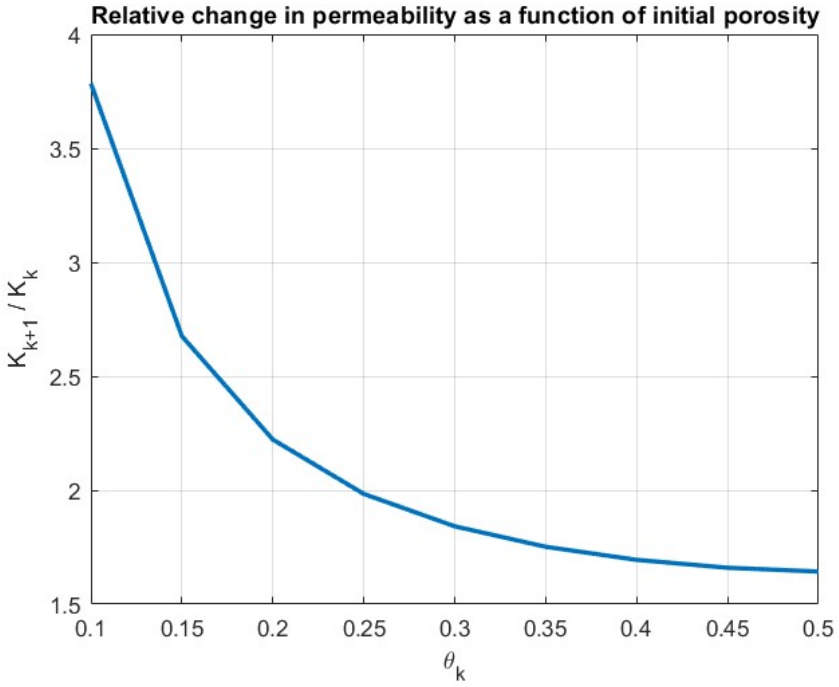

Figure 1. Relative change in permeability as a function of initial porosity.

initial porosity value of 0.43 for all field realizations, regardless of their heterogeneity degree, while the permeability is distributed randomly based on prescribed values of distribution variance and correlation length as explained in Section 2.1 (lines 150–156) in the updated manuscript. While this assumption cannot be seen as rigorous, we argue that it doesn't impact significantly the simulation results, as well as the main conclusions made, since the main point of the manuscript is to capture the essential behavior of the complex coupled process of geochemical weathering, simple enough to not make the reactive model the main issue of the manuscript, but sufficient to be able to draw conclusions about the implications of the ensuing reaction-transport interaction.

We propose to add the following paragraph to the manuscript to clarify this point (lines 156–160 in the updated manuscript):

The constant initial porosity assumption, introduced in order to facilitate the chemical aspects of our reactive trans-

port model, was deemed acceptable, as the purpose of our simplified chemical reaction setup is to capture the qualitative dynamics of the complex process of geochemical weathering, thus making it possible to simulate and analyze the complex reversible behavior using a relatively unsophisticated model.

– My main concern is, however, that the entropies are somewhat abstract properties.

We are sincerely thankful to the Reviewer for pointing out the need to clarify the meaning of both the Shannon and the physical entropies that are employed extensively in the manuscript. In the manuscript, we are looking for the correlation between the emergence and intensification of preferential flowpaths and the dissipation of the useful energy of the system due to different processes, characteristic for chemical weathering, such as chemical reaction, mixing of chemical species and percolation (frictional dissipation due to fluid viscosity). To quantify the intensity of the preferential flowpaths phenomenon (how much is the transport concentrated, or self-organized, within these paths, as opposed to a homogeneous distribution throughout the field), we employ the Shannon entropy, or information entropy – a quantity borrowed from information theory and used, among others, to quantify self-organization in physical systems (see the original paper on this subject by Shannon (1940), as well as Zehe et al (2021) and Shavelzon and Edery (2024) for application to transport self-organization in porous media). On the other hand, to quantify the useful energy dissipation during chemical weathering, we employ the physical entropy, a quantity that, within the framework of nonequilibrium thermodynamics, allows to quantify energy dissipation due to chemical reaction, mixing of chemical species and percolation – see, for instance, Kondepudi and Prigogine (1998). Thus, by employing quantities from seemingly unrelated disciplines, we attempt to correlate between these two parameters in order to obtain a deeper understanding of the phenomenon of preferential flowpaths. These quantities, however, are far from being abstract, but have a precise physical meaning. The main conclusion we arrive at after analyzing both the Shannon entropy of transport self-organization and the physical entropy sources is that a clear correlation is established between the emergence and intensification of preferential flowpaths and the useful energy dissipation due to reaction, mixing and percolation in geochemical systems that involve chemical weathering. The emergence of preferential flowpaths allows the system to reduce this useful energy dissipation rate and, thus, represents an energetically preferred state of the system.

To improve the clarity of presentation of a non-equilibrium thermodynamic framework in the manuscript, we propose adding a short chapter that explains in simple terms the topic of dissipative processes in non-equilibrium thermodynamics to the Supplementary. See **Supplementary 2. Non-equilibrium thermodynamics in a nutshell** in the updated manuscript.

We also propose adding a short section that briefly explains the concept of the Shannon entropy and its use for quantifying self-organization in our physical scenario, along the lines of Section 3.2 and Supplementary 2 in Shavelzon and Edery (2024) (currently, the manuscript draft references this publication, where this subject is treated extensively). See

Section 3.2 in the *updated* manuscript (lines 371—401). Also, notice that references to Supplementary 2 in Shavelzon and Edery (2024), which contains a brief background on the Shannon entropy, are given in the appropriate places in the manuscript. In that way, both the Shannon and the physical entropy, as well as their relevance in our manuscript, are explained in the updated manuscript before any use of them is implemented in the Results. Full text of Supplementary 2 in Shavelzon and Edery (2024) is given in the **Appendix A: Employing Shannon entropy to quantify transport self-organization** in the current document for the reviewer's convenience.

– It all makes sense, but I am still left with the feeling that I do not understand fully what happens in the system. One point is why H+ is associated with the preferential flow paths more closely than H2CO3.

We are sincerely thankful to the Reviewer for pointing out this subject, that has not received a sufficient explanation in the manuscript. Different spatial patterns for dissolution and precipitation reactions, associated with an abundance of H+ and H2CO3 respectively, in reactive flow in heterogeneous / fractured porous media have been reported both experimentally (Liu et al (2005), Jones and Detwiller (2016)) and numerically (Edery et al (2021), Kohlhaas et al (2025), Kaufmann et al (2016), Szawello et al (2024)). For dissolution-dominated flows, such as in our case, dissolution occurs mostly within the preferential flowpaths, characterized by higher permeability and flow velocity and, thus, ample supply of reactant (these paths act as main channels for reactant supply). Higher flow velocity within the paths limits the residence time and, thus, the amount of precipitation within the path itself (which is also limited by the more uniform transport within the path that limits mixing, therefore allowing for less chance to disrupt the local chemical equilibrium). However, at the periphery of the paths, which is less permeable as a rule, residence time increases as well as the chance to disrupt local chemical equilibrium, thus leading to increased precipitation there. Both these processes further enhance the preferential flowpaths by making the paths themselves more permeable by virtue of excessive dissolution there, thus attracting even more reactant within the paths, along with making the periphery of the paths even less permeable via an increased precipitation there. This preferential flowpaths enhancement leads to transport self-organization, or channelization, as attested by the decrease in Shannon entropy over time (see Figure 5 in the updated manuscript).

In our manuscript, we simulate the dissolution-dominated reactive flow scenario by injecting low-pH water into the calcite porous matrix. In our chemical reaction model, dissolution of calcite is associated with an abundance of hydrogen ion H+, therefore it is reasonable that it will self-organize within the preferential flow paths, dominated by the dissolution reaction. On the other hand, H2CO3, responsible for precipitation in our model, is expected to be less associated with the preferential flowpaths but rather to exhibit a more homogeneous distribution due to increased precipitation in the vicinity of these paths. Following the respectable Reviewer's comment, we propose to amend the manuscript by adding this discussion in Results/Conclusions (see lines 485–498 and 688-692 in the updated manuscript).

– In this context, I would find it very helpful to separate the propagation of the reaction front from the changes in the flow pattern. So considering the dynamics of the reaction without taking into account the effect on the permeability. Then

it would be easier to understand what exactly the effect of the changes in permeability is. Maybe the dynamics of the reaction is much faster and it is already clear, but I am not sure.

We sincerely thank the reviewer for suggesting ways to clarify the manuscript. However, we would like to draw the reviewer's attention to the fact that the main point of the manuscript is is the specific interaction between the reactive and transport processes in the calcite porous matrix that leads to the emergence of preferential flowpaths in the matrix. Thus, we will not gain any additional insight by examining the reaction separately from the changes in permeability, as within the particle tracker simulation we cannot account for the reaction without altering the permeability in response to it, since the dissolution-precipitation reaction alters the transport properties of the porous matrix. On the contrary, we aim at showing how the reaction-transport interaction affects both of these processes: the dissolution of calcite, that occurs in the preferential flow paths, intensifies these paths by making them more conductive (as shown by the decrease in Percolative entropy which signifies the decrease in frictional dissipation as the fluid makes its way through the porous matrix) and, therefore, increases the channelization of transport in these paths (as shown by the decreasing Shannon entropy of transport self-organization). On the other hand, this channelization of transport inhibits mixing of chemical species, therefore reducing the overall reaction rate (as shown by Reactive entropy). We are committed to make necessary amendments to Results/Discussion in manuscript to clarify this aspect (see lines 626-637 and 693-704 in the updated manuscript).

– Perhaps it would also be helpful to complement the 2D pictures of the concentrations in Fig. 3 by longitudinal profiles (integrated along the y-axis) in order to see whether the species are just concentrated more or less along the preferential flow paths or also follow strongly different distributions along the x-axis.

We thank again the reviewer for suggesting ways to further clarify the manuscript. The concentration of species along the preferential flowpaths, or, as we refer it in the paper, the intensity of the preferential flowpaths phenomenon (meaning how much is the spatial distribution of the species concentrated, or self-organized, within these paths, as opposed to a homogeneous distribution throughout the field), is quantified in the manuscript using the Shannon entropy (see explanation on this quantity in the text above, as well as in the reply to the last item in the document). These trends are shown in Figure 5 in the updated manuscript: the frames (a)–(b) show the Shannon entropy of spatial distributions of H+ and H2CO3 as a function of distance from inlet at a specific time, while the frames (c)–(d) show the mean value of Shannon entropy of spatial distributions of H+, H2CO3 and the total population over the field as a function of time. In general, the decrease in Shannon entropy of some distribution means an increase in its spatial organization (Zehe et al (2021), Shavelzon and Edery (2024)). The decrease in Shannon entropy with distance from inlet, as well as with an increase in variance of spatial permeability distribution σ_0^2, shows an increase in self-organization of species, meaning that their spatial distribution becomes less homogeneous, and, thus, more of the species find themselves within the preferential flowpaths. The decrease in Shannon entropy with time also shows an increase in self-organization of species as

the time passes, as a result of reaction-transport interaction. We are committed to make necessary amendments to the manuscript to clarify this aspect (see lines 392-401 in Section 3.2 of the updated manuscript, as well as Supplementary 2 in Shavelzon and Edery (2024) - also reprinted in Appendix A in the current document).

– In summary: really interesting stuff, nothing wrong as far as I can see, but the paper would benefit from a more basic and clearer explanation of the model's behavior.

We thank the reviewer for expressing interest in the results presented in the manuscript, as well as for indicating the need to improve the readability of the manuscript, clarifying it and making it more concise. We fully acknowledge this need and are committed to amending the manuscript accordingly. Please find attached the summary of our suggestions regarding improving the overall clarity and readability of the manuscript, organized by chapter. All proposed changes have been implemented in the updated manuscript.

(a) **Abstract**:

Rewritten to better convey the key message of the manuscript regarding the correlation between the transport self-organization and the accompanying dissipative dynamics during chemical weathering, as well as to emphasize the geophysical aspects of chemical weathering and the implications of our study for real-world geophysical scenario of subsurface CO2 sequestration by mineralization (see lines 1–21 in the updated manuscript):

Abstract. *Chemical weathering of soil and rock is a complex geophysical process during which the reaction and transport processes in the porous medium interact, causing erosion of the medium. This process is ubiquitous in geophysical systems and can be encountered, among others, in formation of karst systems, subsurface carbon sequestration and surface weathering of river beds. A common outcome of chemical weathering is the emergence and intensification of preferential flow paths, where the weathering alters the transport properties of the rock, thus creating coupling between transport and reaction. While numerous approaches have been undertaken to simulate this complex interaction, still a need exists for a unified framework able to correlate the emergence of preferential flow paths due to reaction-transport interaction with the associated dissipative dynamics. Here we propose such a framework considering the case of subsurface chemical weathering of calcite porous rock undergoing reversible dissolution-precipitation reaction, and apply non-equilibrium thermodynamics to analyze the ensuing reaction-transport interaction in this geophysical scenario. We identify the entropy generation sources, attributed to the dissipative processes inherent to this physical scenario and show a clear correlation between the emergence and intensification of preferential flow paths and the accompanying dissipative dynamics, where the evolution of the emerging paths leads to a decrease in the free-energy dissipation rate due to flow percolation, mixing of chemical constituents and reaction. This indicates that the emergence of preferential flow paths due to chemical weathering in geophysical systems represents an energetically-preferred state of the system that can be considered a manifes-*

tation of the minimum energy dissipation principle. Our analysis implies that, for a given pressure head, a more homogeneous porous matrix will result in less pronounced preferential flow paths, along with lower flow and higher mineralization rates. On the other hand, for a highly heterogeneous matrix dominant preferential flow paths will be obtained, along with higher flow and lower mineralization rates. Considering these aspects for carbon sequestration where acidified brine leads to carbon mineralization, we conclude that, for a given pressure head, an injection into a more heterogeneous matrix will result in a higher injection rate, while a more homogeneous domain will yield a higher mineralization rate, thus exemplifying the resulting trade-off in the injection strategy.

(b) **Chapter 1 (Introduction)**:

Rewritten to improve clarity of the exposition: beginning from Viewing chemical weathering as a non-equilibrium thermodynamic process, we move to Overall review of analysis of non-equilibrium systems and then to Self-organization as a manifestation of non-equilibrium state. We proceed with Application of non-equilibrium thermodynamics to transport in porous media and conclude with Objectives of our study. See updated manuscript.

(c) **Chapter 2 (Methodology)**:

- A conceptual flowchart added at the beginning of Chapter 2 (Methodology) - see Figure 2 in the current document, as well as Figure 1 in the *updated* manuscript. This flowchart details the various stages of the employed methodology, from creating a realization of hydraulic conductivity field to numerical simulation to calculating the Shannon entropy and the physical entropy sources employing data obtained from simulation. The flowchart also presents graphically the research question of the manuscript, that concerns the correlation between the emergence of preferential flow paths (transport self-organization quantified using Shannon entropy) and the free-energy dissipation due to flow percolation, mixing and reaction (physical entropy sources). Each graphical block (shown by different colors in the flowchart) references the specific section where it is explained in details (section numbers have been adjusted to reflect the suggested manuscript amendments in the updated manuscript). See lines 137–142 in the updated manuscript.
- Section 2.2 (Chemical reaction model) rewritten and expanded to allow for a clearer description of the chemical model and its underlying assumptions. Also, we suggest minor corrections/additions to Chapter 2 as a whole to improve the overall presentation of methodology. See our suggestion for the updated Chapter 2 in the updated manuscript, specifically Section 2.2 (lines 193-221).
- A short section on the Lagrangian particle tracking model validation in 2D added (in Shavelzon and Edery, 2024 the validation was done for the 1D scenario) - see Supplementary 1 in the updated manuscript.
- Abstract terminology throughout the manuscript simplified where possible - such as the Langevin equation paraphernalia (lines 77–85 in the updated manuscript) - as related to purely technical aspects of our study and unnecessary for conveying the key message of the manuscript.

(d) **Chapter 3 (Non-equilibrium thermodynamic framework)**:

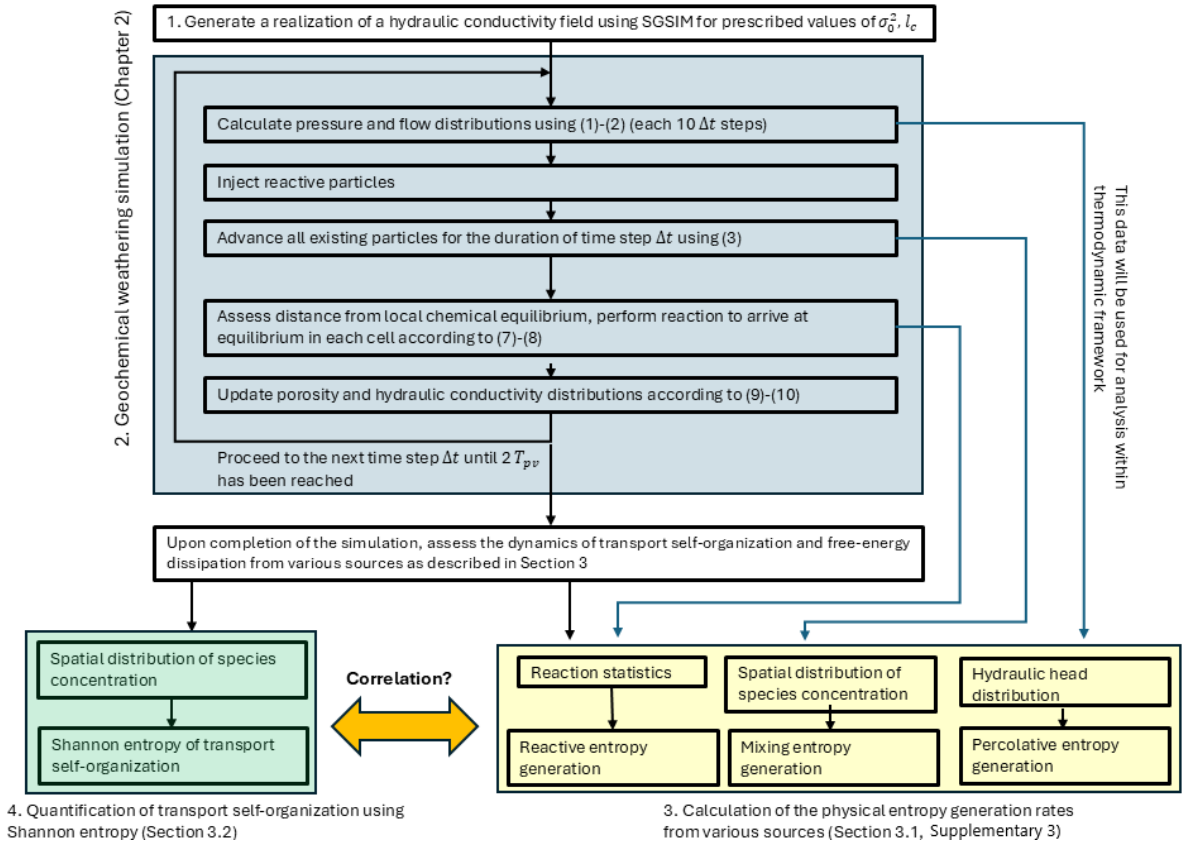

Figure 2. Roadmap chart for the research procedure.

– Section 3.2 (Calculation of entropy generation terms) moved to Supplements, as it basically contains technical details that are not critical for understanding of the manuscript (See Supplementary 3 in the updated manuscript).

– A short chapter that explains in simple terms the topic of dissipative processes in non-equilibrium thermodynamics added to the Supplementary. See Supplementary 2 in the updated manuscript, also Section 3.1 there (lines 282–311).

– A short section added that briefly explains the concept of the Shannon entropy and its use for quantifying self-organization in our physical scenario along the lines of Section 3.2 and Supplementary 2 in Shavelzon and Edery (2024) (currently, the manuscript draft references this publication, where this subject is treated extensively). See Section 3.2 in the updated manuscript (lines 371—401). Also, notice that references to Supplementary 2 in Shavelzon and Edery (2024), which contains a brief background on the Shannon entropy, are given in the appropriate places in the manuscript. In that way, both the Shannon and the physical entropy, as well as their relevance in our manuscript, are explained before any use of them is implemented in the Results. Full text of Supplementary 2 in

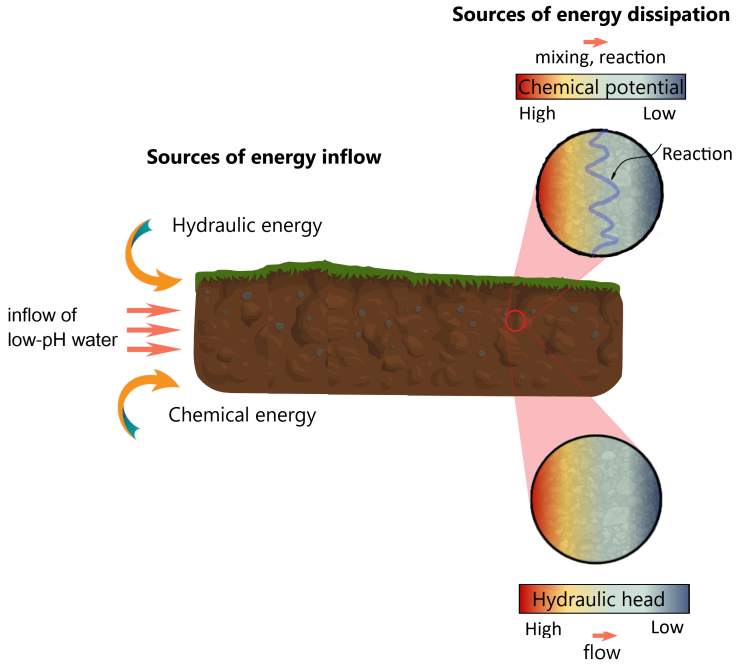

Figure 3. Sources of inflow and dissipation of free energy in subsurface reactive flow.

Shavelzon and Edery (2024) is given in the **Appendix A: Employing Shannon entropy to quantify transport self-organization** in the current document.

- Figure that shows graphically the sources of inflow and dissipation of free energy in subsurface reactive flow replaced with an improved version that explains more clearly the sources of free-energy inlfow into the system and its dissipation (see Figure 3 in the current document, as well as Figure 2 in the *updated* manuscript). This figure visualizes the main result of Section 3.1: entropy generation, which is directly related to dissipation of the free-energy of the system, occurs in dissipative processes where the gradient of a thermodynamic potential drives the thermodynamic flux. Thus, the gradient of hydraulic head drives the mass flux, the gradient of the chemical potential drives the molar fluxes of the chemical species and the partial molar Gibbs energy drives the extent of reaction. See Section 3.1 (lines 283–310) and Supplementary 2 in the updated manuscript for detailed explanation.
- Abstract terminology throughout the manuscript simplified where possible - such as differential operators used in the exposition of non-equilibrium thermodynamic framework (lines 345–360 in the updated manuscript) - as related to purely technical aspects of our study and unnecessary for conveying the key message of the manuscript.

(e) **Section 4 (Results)**:

- Shortened by (a) moving Section 4.2 (Statistical analysis of the transport properties of the porous medium) to Supplements, as it contains results that are tangential to the main message of the manuscript (see Supplementary

4 in the updated manuscript), and (b) the discussion of the absolute Reactive entropy removed altogether, now focusing on discussing the useful Reaction entropy, as this quantity can be measured experimentally.

- Section rewritten to allow for a clearer and more concise analysis of the obtained results, as well as their interpretation in terms of the correlation between transport self-organization in the field and the accompanying dissipative dynamics.
- A concluding Section added that frames our findings in the broader implications for real-world geochemical systems on an example of CO2 sequestration by mineralization, as a highly relevant example of an interaction between transport and dissolution-precipitation reaction (see Section 4.3, lines 651-678 in the updated manuscript). The proposed Section reads:

4.3 Implications for subsurface carbon sequestration by mineralization

The relevance of our study can be exemplified on a case of subsurface carbon sequestration by mineralization that involves injection of either dissolved or supercritical CO_2 into reactive rocks, particularly mafic, ultramafic or carbonate, leading to CO_2 mineralization and fixing carbon in the subsurface with little risk of escape to the atmosphere (Snaebjornsdottir et al., 2020, Ruprecht and Falta, 2012). For the supercritical CO_2 injection, CO_2 solubility in brine increases with pressure as the solute advances deeper into subsurface, thus leading to acidification of the brine layer in contact with the supercritical CO_2 (Pradhan et al., 2025). This enriched layer, having a typical pH of 3–5, is denser than the surrounding resident brine, thus creating a negative buoyancy. This facilitates the transport of acidic brine downwards in the porous matrix (Ahmad et al., 2016). This acidic solution promotes the dissolution of silicate minerals, facilitating the subsequent CO_2 mineralization by (a) consuming the hydrogen ions, which neutralizes the acidic solution and facilitates precipitation of carbonate minerals, and (b) providing cations that react with the dissolved CO_2 to form stable carbonate minerals (Snaebjornsdottir et al., 2020). Thus, a complex reaction-transport interaction ensues following CO_2 injection into subsurface, where the rate of CO_2 mineralization is strongly affected by the preferential flow paths, either existing in the subsurface or emerged/altered due to dissolution of silicate minerals. Although CO_2 mineralization in mafic rocks involves dissolved cations different from Ca^{2+} as in our study (Mg^{2+}, Fe^{2+}, etc.), nevertheless the mechanism follows the same traits, thus allowing us to speculate on this subject based on our study.

The existence of dominant preferential flow paths and their intensification due to reaction-transport interaction can facilitate CO_2 injection and may be favorable for carbon sequestration as it allows decreasing the hydraulic power per unit flow rate required for CO_2 injection (Oldenburg, 2001). This is confirmed by Figure 6c in the updated manuscript that shows a decrease in the normalized Percolative entropy with the intensification of preferential flow paths due to either an increase in the field heterogeneity σ_0^2 or the computational time $\tilde{t}$, which signifies a decrease in the free-energy dissipation due to flow percolation. On the other hand, for CO_2 mineralization, the existence of dominant preferential flow paths may inhibit the overall extent of reaction per unit flow rate due to

channelization of reactive species that limits their exposure to calcite (Harrison et al., 2016). This is confirmed by Figure 6a that shows a decrease in the normalized Reactive entropy with the intensification of preferential flow paths, signifying a decrease in the overall reaction rate. To summarize, for a given pressure head, an injection into a more heterogeneous matrix will result in a higher injection rate, while a more homogeneous domain will yield a higher mineralization rate, thus exemplifying the resulting trade-off in the injection strategy.

(f) **Conclusions**:

Rewritten to better convey the key message of the manuscript regarding the correlation between the transport self-organization and the accompanying dissipative dynamics during chemical weathering, as well as to emphasize the geophysical aspects of chemical weathering and the implications of our study for real-world geophysical scenario of subsurface CO2 sequestration by mineralization.

Appendix A: Employing Shannon entropy to quantify transport self-organization

To revise the basic concept of information entropy, let us consider a single probabilistic event, having a number of possible outcomes that are assumed equally probable. For example, in the case of a single symbol transmitted in the Morse code, we have two possible outcomes (realizations) for this event - a dash and a dot (omitting the intermission between the transmitted letters). Employing the indices 0 and 1 to denote parameters before and after the event realization, initially, we have $N_0 = 2$ equally possible outcomes of the message transmission event and zero initial information $I_0 = 0$. Following the transmission of a single symbol, we have a single realization of the event - a dash or a dot, thus $N_1 = 1$, and a non zero information due to the receipt of a symbol $I_1 \neq 0$.

In case of a sequence of events enumerated $1...n$, having a respective number of outcomes $N_{0_1}, N_{0_2}, ..., N_{0_n}$ (consider a word that consists of n symbols in the Morse alphabet), the total number of possible outcomes is $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}$. Intuitively, we would expect the information measure to be an additive parameter so that the amount of information contained in a word transmitted with the help of the Morse code would be equal to the sum of the amounts of information for each symbol that constitutes the word, that is $I(N) = I(N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}) = I(N_{0_1}) + I(N_{0_2}) + ... + I(N_{0_n})$. This can be fulfilled by choosing $I = b \ln N$, where b is an arbitrary constant parameter that amounts to a choice of a unit of measure (in fact, Shannon (1948) gave a formal proof that the logarithm function is the only possible relation between I and N that possesses, in addition to additivity, also continuity and monotonicity properties). For a binary system that consists of only two symbols, such as the dash and the dot in the Morse alphabet, a transmitted word of a total n symbols has $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n} = 2^n$ possible realizations. Taking a single transmitted symbol as one unit of information, we demand that $I = b \ln N = n$ to obtain $b = \log_2 e$ and $I = \log_2 N$. Since a single position in a sequence of symbols in a binary system is defined as a bit, the corresponding units of information I will be called $bits$ (an abbreviation from

binary digit).

Now, assume that each of the final amount of different symbols that constitute a message has its own relative occurrence frequency (the respective probability of finding a specific symbol at a specific place in a sequence), such as the case of different letters in an alphabet. In the case of a Morse code, assume that the transmitted n-symbol word consists of n_1 dashes and n_2 dots, so that $n_1 + n_2 = n$. Using some results from combinatorics, it can be shown that

$$S = I/n = -\Sigma_i \, p_i \log_2 p_i \tag{1}$$

where S is the information entropy (also referred to as the Shannon entropy) per symbol and $p_i = n_i/n, \; i = 1, 2$ are the relative occurrence frequencies of both symbols. Maximum Shannon entropy obtained during the transmission of a message is when the relative occurrence frequency of each symbol is identical $p = 1/2$. It is easily shown that this maximum value equals to $S_{max} = -\log_2 p = 1$. The relation (1) can be easily generalized for any number of possible outcomes per event. Thus, a definition of the information entropy is obtained that possesses an additivity property similar to physical properties such as entropy, energy, and mass. An example that may be seen as a consequence of the results obtained with the help of the information theory is that in modern communication methods, the more common alphabet letters are encoded in such a way that their information content is minimized in order to facilitate the transmission process. Thus, in a Morse code, a letter E is encoded by a single dot, while J is a dot followed by three dashes. For more details on the topic of Shannon entropy, see Shannon (1948).

This definition resembles the definition physical entropy in statistical mechanics, as defined by Gibbs, where the logarithm in Eq. (1) is to the base of e and the sum is multiplied by the Boltzmann constant. The statistical definition of physical entropy characterizes the number of possible microstates of a system that are consistent with its macroscopic thermodynamic properties, which constitute the macrostate of the system. Thus, in the case of a gas consisting of a large number of molecules in a container, a microstate of the system consists of the position and momentum of each molecule as it moves within the container, colliding with other molecules and container walls. A multitude of such microstates correspond to a single macroscopic state of the system, defined by its pressure and temperature. The parameter p_i in this case corresponds to a probability that a microstate i occurs during the system's fluctuations. According to the second law of Thermodynamics, the entropy of an isolated system reaches its maximum value at equilibrium, where gradients of thermodynamic parameters are depleted by dissipative forces and the measure of order in the system is at its minimum. In this case, each microstate is equally likely and p_i is simply the inverse of the total number of microstates (Kondepudi and Prigogine, 1998). Returning to the context of communication theory, maximum entropy is obtained during the transmission of a message of a length n when an alphabet with the largest number of symbols is employed, and the relative occurrence frequency of each symbol is identical.

To characterize the emergence and evolution of transport self-organization in a computational field as the dissolution-

precipitation reactive processes in the field advance, we adopt a straightforward use of the Shannon entropy, in a similar vein to Zehe et al (2021) and Shavelzon and Edery (2024), where it was employed in the context of characterizing self-organization in non-reactive flow in a heterogeneous porous medium. We calculate the Shannon entropy of particle distribution in the direction transverse to flow at a dimensionless time $\tilde{t}$ as a function of distance from the inlet x, $S(x,\tilde{t})$, using the same formula as in (1), reprinted here as

$$S(x,\tilde{t}) = -\Sigma_i p_i \log_2 p_i \tag{2}$$

where $p_i = N_i/N_{tot},\ i = 1...N_y$ is the relative concentration distribution at $x,\tilde{t}$ in the direction transverse to flow (here, N_i is the current number of particles of a specific specie in the i-th cell in the vertical direction at x and N_{tot} is the total number of particles of that specie in all cells at x, taken at a dimensionless time $\tilde{t}$). This quantity has an upper bound of $S_{max} = \log_2 N_y$, corresponding to the state of maximum entropy, or homogeneity of transport in the field, where the same number of particles has visited each of the N_y computational cells at a given distance from inlet x; the obvious lower bound of 0 corresponds to the state of maximum transport spatial organization in the field, namely all particles follow a single preferential flow path (Zehe et al (2021) and Shavelzon and Edery (2024)).

References:

- Shavelzon and Edery (2024), Shannon entropy of transport self-organization due to dissolution–precipitation reaction at varying Peclet numbers in initially homogeneous porous media,
- Shannon (1948), A Mathematical Theory Of Communication.
- Zehe et al (2021), Preferential Pathways for Fluid and Solutes in Heterogeneous Groundwater Systems.
- Edery and Stolar (2021), Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields.
- Edery et al (2011), Dissolution and precipitation dynamics during dedolomitization.
- Singurindy and Berkowitz (2003), Flow, dissolution, and precipitation in dolomite.
- Al-Khulaifi et al(2017), Reaction Rates in Chemically Heterogeneous Rock: Coupled Impact of Structure and Flow Properties Studied by X-ray Microtomography
- Manahan (2000), Environmental Chemistry (9th edn).
- Amorsson (1981), Mineral Deposition From Icelandic Geothermal Waters: Environmental and Utilization Problems.
- Snaebjornsdottir et al (2020), Carbon dioxide storage through mineral carbonation.
- Ruprecht and Falta (2012), COMPARISON OF SUPERCRITICAL AND DISSOLVED CO2 INJECTION SCHEMES.
- Pradhan et al (2025), Determination of CO2 solubility in brines and produced waters of various salinities for CO2 EOR and storage applications.

- Ahmad et al (2016), Injection of CO2-saturated brine in geological reservoir: A way to enhanced storage safety.
- Oldenburg et al (2001), Carbon Sequestration with Enhanced Gas Recovery: Identifying Candidate Sites for Pilot Study.
- Cao et al (2013), Dynamic alterations in wellbore cement integrity due to geochemical reactions in CO2-rich environments.
- Haugen et al (2023), Multi-scale dissolution dynamics for carbon sequestration in carbonate rock samples.
- Harrison et al (2015), The impact of evolving mineral–water–gas interfacial areas on mineral–fluid reaction rates in unsaturated porous media
- Kondepudi and Prigogine (1998), Modern Thermodynamics: From Heat Engines to Dissipative Structures.
- Kaufmann et al (2016), Dissolution and precipitation of fractures in soluble rock
- Szawello et al (2024), Quantifying dissolution dynamics in porous media using a spatial flow focusing profile.
- Liu et al (2005), Dissolution-induced preferential flow in a limestone fracture.
- Jones and Detwiller (2016), Fracture sealing by mineral precipitation: The role of small-scale mineral heterogeneity.
- Kohlhaas et al (2025), Numerical Investigation of Preferential Flow Paths in Enzymatically Induced Calcite Precipitation supported by Bayesian Model Analysis.
- Deutsch (1997), GSLIB Geostatistical Software Library and User's Guide.
- Morse and Mackenzie (1990), Geochemistry of Sedimentary Carbonates
- Kreft and Zuber (1978), On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions.
- Perez et al (2019), Reactive Random Walk Particle Tracking and Its Equivalence With the Advection-Diffusion-Reaction Equation.
- Risken (1996), The Fokker-Planck Equation: Methods of Solution and Applications.
- Press et al (1992), Numerical Recipes in C: The Art of Scientific Computing.
- Kloeden (1992), Numerical solution of stochastic differential equations.
- Domenico and Schwartz, Physical and Chemical Hydrogeology, 2nd Edition.
- Le Borgne et al (2008), Lagrangian Statistical Model for Transport in Highly Heterogeneous Velocity Fields.
- Gudagninin and Neumann (1999), Nonlocal and localized analyses of conditional mean steady state flow in bounded, randomly nonuniform domains: 1. Theory and computational approach.

Linking chemical weathering, evolution of preferential flow paths and transport self-organization in porous media using non-equilibrium thermodynamics

Evgeny Shavelzon[1], Erwin Zehe[2], and Yaniv Edery[1]

[1]Faculty of Civil and Environmental Engineering, Technion - Israeli Institute of Technology, Haifa, Israel
[2]Karlsruhe Institute of Technology (KIT), Institute of Water and River Basin Management, Karlsruhe, Germany

Correspondence: Yaniv Edery(yanivedery@technion.ac.il)

Replies to Reviewer 2

Reviewer 2

The manuscript by Shavelzon et al. aims to establish a novel connection between chemical weathering, transport self-organization, and non-equilibrium thermodynamics by using a particle-tracking reactive transport model in 2D porous media with varying heterogeneity. This topic would likely be of interest to researchers seeking better frameworks to describe the formation of preferential pathways in the subsurface driven by water-rock interactions. However, the current version of the manuscript is difficult to read and interpret, due to excessive technical density, insufficient narrative structure, and limited discussion of the model assumptions and broader scientific implications. I think major revisions are needed before the manuscript can be considered for publication.

We thank the reviewer for recognizing the potential relevance of our work to the HESS readership. The comments from the reviewer are well received and were extremely helpful in clarifying and improving our study. We are also thankful to the reviewer for indicating the need to improve the readability of the manuscript and its relevance for the geophysical community by clarifying it and making it more concise, as well as by discussing the broader implications of our research for real-world geochemical systems. We fully acknowledge this need and are committed to amending the manuscript accordingly.

1. Excessive length, technical complexity and abstract terminology. The paper dives into lengthy derivations and modeling details early on (especially Sections 2-3), but without sufficient explanations for why this framework matters or what the reader should expect to learn. This makes it difficult to parse how the pieces fit together—especially for readers unfamiliar with entropy generation in porous media. A conceptual figure or roadmap either at the end of the Introduction or at the beginning of the Methods would help guide the readers.

We sincerely thank the reviewer for pointing out the need to improve the readability of the manuscript, clarify it and make it more concise. We fully acknowledge this need and are committed to amending the manuscript accordingly. Please find attached the summary of our suggestions regarding shortening the manuscript, as well as improving its overall clarity and readability, organized by chapter. All of these suggestions have been implemented in the updated manuscript draft.

(a) **Abstract**:

Rewritten to better convey the key message of the manuscript regarding the correlation between the transport self-organization and the accompanying dissipative dynamics during chemical weathering, as well as to emphasize the geophysical aspects of chemical weathering and the implications of our study for real-world geophysical scenario of subsurface CO2 sequestration by mineralization (see lines 1–21 in the updated manuscript):

Abstract. *Chemical weathering of soil and rock is a complex geophysical process during which the reaction and transport processes in the porous medium interact, causing erosion of the medium. This process is ubiquitous in geophysical systems and can be encountered, among others, in formation of karst systems, subsurface carbon sequestration and surface weathering of river beds. A common outcome of chemical weathering is the emergence and intensification of preferential flow paths, where the weathering alters the transport properties of the rock, thus creating coupling between transport and reaction. While numerous approaches have been undertaken to simulate this complex interaction, still a need exists for a unified framework able to correlate the emergence of preferential flow paths due to reaction-transport interaction with the associated dissipative dynamics. Here we propose such a framework considering the case of subsurface chemical weathering of calcite porous rock undergoing reversible dissolution-precipitation reaction, and apply non-equilibrium thermodynamics to analyze the ensuing reaction-transport interaction in this geophysical scenario. We identify the entropy generation sources, attributed to the dissipative processes inherent to this physical scenario and show a clear correlation between the emergence and intensification of preferential flow paths and the accompanying dissipative dynamics, where the evolution of the emerging paths leads to a decrease in the free-energy dissipation rate due to flow percolation, mixing of chemical constituents and reaction. This indicates that the emergence of preferential flow paths due to chemical weathering in geophysical systems represents an energetically-preferred state of the system that can be considered a manifestation of the minimum energy dissipation principle. Our analysis implies that, for a given pressure head, a more homogeneous porous matrix will result in less pronounced preferential flow paths, along with lower flow and higher mineralization rates. On the other hand, for a highly heterogeneous matrix dominant preferential flow paths will be obtained, along with higher flow and lower mineralization rates. Considering these aspects for carbon sequestration where acidified brine leads to carbon mineralization, we conclude that, for a given pressure head, an injection*

into a more heterogeneous matrix will result in a higher injection rate, while a more homogeneous domain will yield a higher mineralization rate, thus exemplifying the resulting trade-off in the injection strategy.

(b) **Chapter 1 (Introduction)**:

Rewritten to improve clarity of the exposition: beginning from Viewing chemical weathering as a non-equilibrium thermodynamic process, we move to Overall review of analysis of non-equilibrium systems and then to Self-organization as a manifestation of non-equilibrium state. We proceed with Application of non-equilibrium thermodynamics to transport in porous media and conclude with Objectives of our study. See updated manuscript.

(c) **Chapter 2 (Methodology)**:

– A conceptual flowchart added at the beginning of Chapter 2 (Methodology) - see Figure 1 in the current document, as well as Figure 1 in the *updated* manuscript. This flowchart details the various stages of the employed methodol-

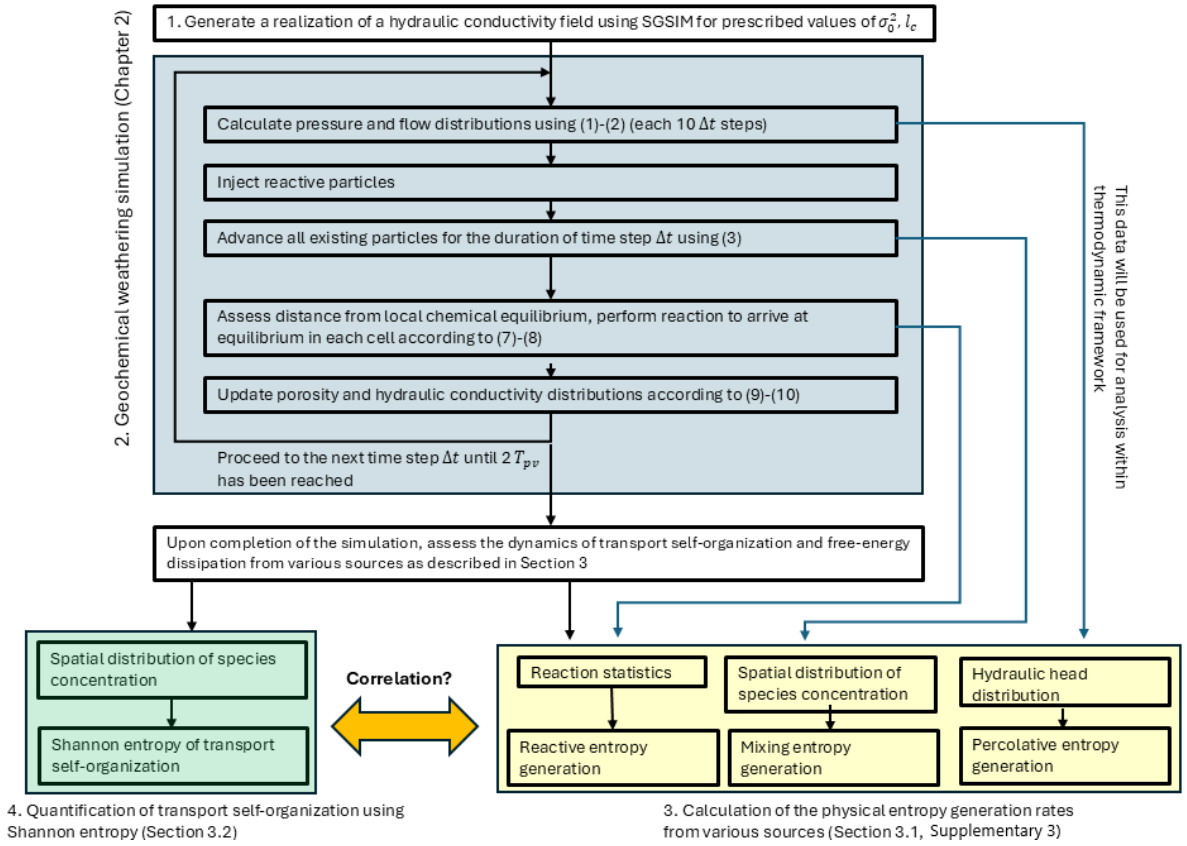

Figure 1. Roadmap chart for the research procedure.

ogy, from creating a realization of hydraulic conductivity field to numerical simulation to calculating the Shannon

entropy and the physical entropy sources employing data obtained from simulation. The flowchart also presents graphically the research question of the manuscript, that concerns the correlation between the emergence of preferential flow paths (transport self-organization quantified using Shannon entropy) and the free-energy dissipation due to flow percolation, mixing and reaction (physical entropy sources). Each graphical block (shown by different colors in the flowchart) references the specific section where it is explained in details (section numbers have been adjusted to reflect the suggested manuscript amendments in the updated manuscript). See lines 137–142 in the updated manuscript.

- Section 2.2 (Chemical reaction model) rewritten and expanded to allow for a clearer description of the chemical model and its underlying assumptions. Also, we suggest minor corrections/additions to Chapter 2 as a whole to improve the overall presentation of methodology. See our suggestion for the updated Chapter 2 in the updated manuscript, specifically Section 2.2 (lines 193-221).
- A short section on the Lagrangian particle tracking model validation in 2D added (in Shavelzon and Edery, 2024 the validation was done for the 1D scenario) - see Supplementary 1 in the updated manuscript.
- Abstract terminology throughout the manuscript simplified where possible - such as the Langevin equation paraphernalia (lines 77–85 in the updated manuscript) - as related to purely technical aspects of our study and unnecessary for conveying the key message of the manuscript.

(d) **Chapter 3 (Non-equilibrium thermodynamic framework)**:

- Section 3.2 (Calculation of entropy generation terms) moved to Supplements, as it basically contains technical details that are not critical for understanding of the manuscript (See Supplementary 3 in the updated manuscript).
- A short chapter that explains in simple terms the topic of dissipative processes in non-equilibrium thermodynamics added to the Supplementary. See Supplementary 2 in the updated manuscript, also Section 3.1 there (lines 282–311).
- A short section added that briefly explains the concept of the Shannon entropy and its use for quantifying self-organization in our physical scenario along the lines of Section 3.2 and Supplementary 2 in Shavelzon and Edery (2024) (currently, the manuscript draft references this publication, where this subject is treated extensively). See Section 3.2 in the updated manuscript (lines 371—401). Also, notice that references to Supplementary 2 in Shavelzon and Edery (2024), which contains a brief background on the Shannon entropy, are given in the appropriate places in the manuscript. In that way, both the Shannon and the physical entropy, as well as their relevance in our manuscript, are explained before any use of them is implemented in the Results. Full text of Supplementary 2 in Shavelzon and Edery (2024) is given in the **Appendix A: Employing Shannon entropy to quantify transport self-organization** in the current document.
- Figure that shows graphically the sources of inflow and dissipation of free energy in subsurface reactive flow replaced with an improved version that explains more clearly the sources of free-energy inlfow into the system

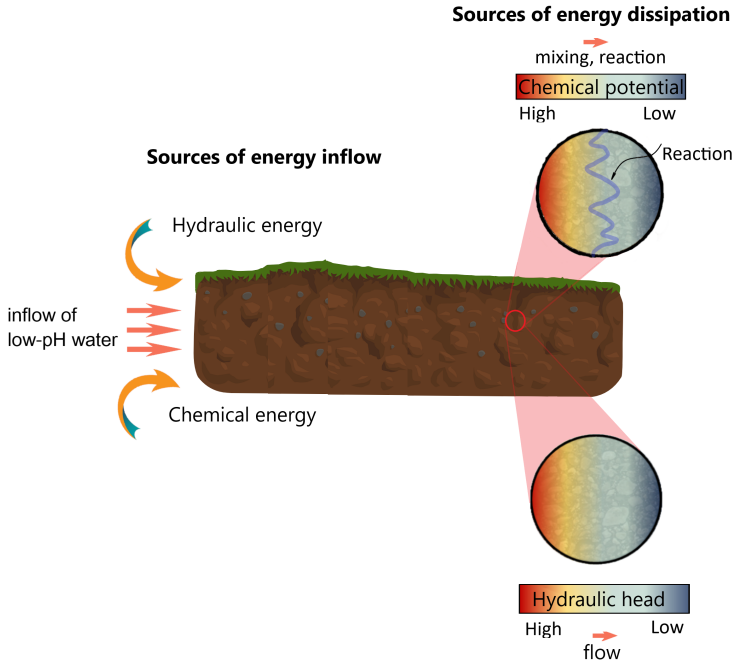

Figure 2. Sources of inflow and dissipation of free energy in subsurface reactive flow.

and its dissipation (see Figure 2 in the current document, as well as Figure 2 in the *updated* manuscript). This figure visualizes the main result of Section 3.1: entropy generation, which is directly related to dissipation of the free-energy of the system, occurs in dissipative processes where the gradient of a thermodynamic potential drives the thermodynamic flux. Thus, the gradient of hydraulic head drives the mass flux, the gradient of the chemical potential drives the molar fluxes of the chemical species and the partial molar Gibbs energy drives the extent of reaction. See Section 3.1 (lines 283–310) and Supplementary 2 in the updated manuscript for detailed explanation.

- Abstract terminology throughout the manuscript simplified where possible - such as differential operators used in the exposition of non-equilibrium thermodynamic framework (lines 345–360 in the updated manuscript) - as related to purely technical aspects of our study and unnecessary for conveying the key message of the manuscript.

(e) **Section 4 (Results)**:

- Shortened by (a) moving Section 4.2 (Statistical analysis of the transport properties of the porous medium) to Supplements, as it contains results that are tangential to the main message of the manuscript (see Supplementary 4 in the updated manuscript), and (b) the discussion of the absolute Reactive entropy removed altogether, now focusing on discussing the useful Reaction entropy, as this quantity can be measured experimentally.

– Section rewritten to allow for a clearer and more concise analysis of the obtained results, as well as their interpretation in terms of the correlation between transport self-organization in the field and the accompanying dissipative dynamics.

– A concluding Section added that frames our findings in the broader implications for real-world geochemical systems on an example of CO2 sequestration by mineralization, as a highly relevant example of an interaction between transport and dissolution-precipitation reaction (see Section 4.3, lines 651-678 in the updated manuscript). The proposed Section reads:

4.3 Implications for subsurface carbon sequestration by mineralization

The relevance of our study can be exemplified on a case of subsurface carbon sequestration by mineralization that involves injection of either dissolved or supercritical CO_2 into reactive rocks, particularly mafic, ultramafic or carbonate, leading to CO_2 mineralization and fixing carbon in the subsurface with little risk of escape to the atmosphere (Snaebjornsdottir et al., 2020, Ruprecht and Falta, 2012). For the supercritical CO_2 injection, CO_2 solubility in brine increases with pressure as the solute advances deeper into subsurface, thus leading to acidification of the brine layer in contact with the supercritical CO_2 (Pradhan et al., 2025). This enriched layer, having a typical pH of 3–5, is denser than the surrounding resident brine, thus creating a negative buoyancy. This facilitates the transport of acidic brine downwards in the porous matrix (Ahmad et al., 2016). This acidic solution promotes the dissolution of silicate minerals, facilitating the subsequent CO_2 mineralization by (a) consuming the hydrogen ions, which neutralizes the acidic solution and facilitates precipitation of carbonate minerals, and (b) providing cations that react with the dissolved CO_2 to form stable carbonate minerals (Snaebjornsdottir et al., 2020). Thus, a complex reaction-transport interaction ensues following CO_2 injection into subsurface, where the rate of CO_2 mineralization is strongly affected by the preferential flow paths, either existing in the subsurface or emerged/altered due to dissolution of silicate minerals. Although CO_2 mineralization in mafic rocks involves dissolved cations different from Ca^{2+} as in our study (Mg^{2+}, Fe^{2+}, etc.), nevertheless the mechanism follows the same traits, thus allowing us to speculate on this subject based on our study.

The existence of dominant preferential flow paths and their intensification due to reaction-transport interaction can facilitate CO_2 injection and may be favorable for carbon sequestration as it allows decreasing the hydraulic power per unit flow rate required for CO_2 injection (Oldenburg, 2001). This is confirmed by Figure 6c in the updated manuscript that shows a decrease in the normalized Percolative entropy with the intensification of preferential flow paths due to either an increase in the field heterogeneity σ_0^2 or the computational time $\tilde{t}$, which signifies a decrease in the free-energy dissipation due to flow percolation. On the other hand, for CO_2 mineralization, the existence of dominant preferential flow paths may inhibit the overall extent of reaction per unit flow rate due to channelization of reactive species that limits their exposure to calcite (Harrison et al., 2016). This is confirmed by Figure 6a that shows a decrease in the normalized Reactive entropy with the intensification of preferential flow

paths, signifying a decrease in the overall reaction rate. To summarize, for a given pressure head, an injection into a more heterogeneous matrix will result in a higher injection rate, while a more homogeneous domain will yield a higher mineralization rate, thus exemplifying the resulting trade-off in the injection strategy.

(f) **Conclusions**:

Rewritten to better convey the key message of the manuscript regarding the correlation between the transport self-organization and the accompanying dissipative dynamics during chemical weathering, as well as to emphasize the geophysical aspects of chemical weathering and the implications of our study for real-world geophysical scenario of subsurface CO2 sequestration by mineralization.

2. Unclear assumptions in reactive transport setup and their implications for the conclusions. The authors employ a simplified reactive system consisting of only two solute species (H+ and H2CO3) and a single dissolution–precipitation reaction involving calcite. Important geochemical complexities, such as full aqueous speciation (e.g., bicarbonate, carbonate), are omitted. I think it is necessary to clarify the rationale for these assumptions and discuss their implications for the applicability of results to real-world weathering environments.

We are sincerely thankful to the reviewer for indicating the need to provide a clear explanation for the origins of our chemical reaction model. This simplified chemical representation follows previous work by Edery et al. (2011), where this formulation is treated extensively, and was later employed in Edery et al. (2021) and Shavelzon and Edery (2024). The purpose of this simplified chemical reaction setup is to capture the qualitative dynamics of the complex process of geochemical weathering, thus making it possible to simulate and analyze the complex reversible behavior using a relatively unsophisticated model. The somewhat brief description of the model given in the manuscript follows from the desire to shorten the manuscript length, therefore a reference to Shavelzon and Edery (2024) was given in the beginning of Section 2. To allow for a clearer description of the chemical model, we propose dedicating Section 2.2 solely to the chemical reaction model, rewriting and expanding it, and putting the description of the kinetic aspects and reaction-transport interaction implementation in Section 2.3. Also, we suggest minor corrections/additions to Chapter 2 as a whole to improve the overall presentation of methodology. See our suggestion for the updated Chapter 2 in the updated manuscript (specifically, see Section 2.2 in lines 193-221).

3. Conclusions are too technically narrow. It would better for the authors to frame their findings in the broader implications for real-world geochemical systems, such as rock weathering in karst systems or channelization in CO2-enhanced weathering. Discussing such applications would help connect the modeling results to field-scale processes and enhance the overall significance of the study.

We again thank the reviewer for indicating the necessity to broaden the implications of our study to real-world geochemical processes and propose discussing the implications of the study on an example of subsurface CO2 sequestration

by mineralization, as a highly relevant example of an interaction between transport and dissolution-precipitation reaction. A concluding Section was added to Results that frames our findings in the broader implications for real-world geochemical systems on an example of CO2 sequestration by mineralization, as a highly relevant example of an interaction between transport and dissolution-precipitation reaction (see our repl to the previous item in the current document, as well as Section 4.3, lines 651-678 in the updated manuscript).

4. Minor comments:

   - Abstract, Line 2: "that" -> "which"; add "the" before "emergence".
   - Introduction, Line 17: It is not appropriate to refer to chemical weathering as a geophysical phenomenon. Consider revising to “geochemical process”.
   - Line 663: typo "expend Figure 8biture for the network"

We again thank the reviewer for indicating these typos. These will be fixed in the updated draft.

Appendix A: Employing Shannon entropy to quantify transport self-organization

To revise the basic concept of information entropy, let us consider a single probabilistic event, having a number of possible outcomes that are assumed equally probable. For example, in the case of a single symbol transmitted in the Morse code, we have two possible outcomes (realizations) for this event - a dash and a dot (omitting the intermission between the transmitted letters). Employing the indices 0 and 1 to denote parameters before and after the event realization, initially, we have $N_0 = 2$ equally possible outcomes of the message transmission event and zero initial information $I_0 = 0$. Following the transmission of a single symbol, we have a single realization of the event - a dash or a dot, thus $N_1 = 1$, and a non zero information due to the receipt of a symbol $I_1 \neq 0$.

In case of a sequence of events enumerated $1...n$, having a respective number of outcomes $N_{0_1}, N_{0_2}, ..., N_{0_n}$ (consider a word that consists of n symbols in the Morse alphabet), the total number of possible outcomes is $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}$. Intuitively, we would expect the information measure to be an additive parameter so that the amount of information contained in a word transmitted with the help of the Morse code would be equal to the sum of the amounts of information for each symbol that constitutes the word, that is $I(N) = I(N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}) = I(N_{0_1}) + I(N_{0_2}) + ... + I(N_{0_n})$. This can be fulfilled by choosing $I = b \ln N$, where b is an arbitrary constant parameter that amounts to a choice of a unit of measure (in fact, Shannon (1948) gave a formal proof that the logarithm function is the only possible relation between I and N that possesses, in addition to additivity, also continuity and monotonicity properties). For a binary system that consists of only two symbols, such as the dash and the dot in the Morse alphabet, a transmitted word of a total n symbols has $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n} = 2^n$ possible realizations. Taking a single transmitted symbol as one unit of information, we demand that $I = b \ln N = n$ to obtain $b = \log_2 e$

and $I = \log_2 N$. Since a single position in a sequence of symbols in a binary system is defined as a bit, the corresponding units of information I will be called $bits$ (an abbreviation from *binary digit*).

Now, assume that each of the final amount of different symbols that constitute a message has its own relative occurrence frequency (the respective probability of finding a specific symbol at a specific place in a sequence), such as the case of different letters in an alphabet. In the case of a Morse code, assume that the transmitted n-symbol word consists of n_1 dashes and n_2 dots, so that $n_1 + n_2 = n$. Using some results from combinatorics, it can be shown that

$$S = I/n = -\Sigma_i \, p_i \log_2 p_i \tag{1}$$

where S is the information entropy (also referred to as the Shannon entropy) per symbol and $p_i = n_i/n, \; i = 1, 2$ are the relative occurrence frequencies of both symbols. Maximum Shannon entropy obtained during the transmission of a message is when the relative occurrence frequency of each symbol is identical $p = 1/2$. It is easily shown that this maximum value equals to $S_{max} = -\log_2 p = 1$. The relation (1) can be easily generalized for any number of possible outcomes per event. Thus, a definition of the information entropy is obtained that possesses an additivity property similar to physical properties such as entropy, energy, and mass. An example that may be seen as a consequence of the results obtained with the help of the information theory is that in modern communication methods, the more common alphabet letters are encoded in such a way that their information content is minimized in order to facilitate the transmission process. Thus, in a Morse code, a letter E is encoded by a single dot, while J is a dot followed by three dashes. For more details on the topic of Shannon entropy, see Shannon (1948).

This definition resembles the definition physical entropy in statistical mechanics, as defined by Gibbs, where the logarithm in Eq. (1) is to the base of e and the sum is multiplied by the Boltzmann constant. The statistical definition of physical entropy characterizes the number of possible microstates of a system that are consistent with its macroscopic thermodynamic properties, which constitute the macrostate of the system. Thus, in the case of a gas consisting of a large number of molecules in a container, a microstate of the system consists of the position and momentum of each molecule as it moves within the container, colliding with other molecules and container walls. A multitude of such microstates correspond to a single macroscopic state of the system, defined by its pressure and temperature. The parameter p_i in this case corresponds to a probability that a microstate i occurs during the system's fluctuations. According to the second law of Thermodynamics, the entropy of an isolated system reaches its maximum value at equilibrium, where gradients of thermodynamic parameters are depleted by dissipative forces and the measure of order in the system is at its minimum. In this case, each microstate is equally likely and p_i is simply the inverse of the total number of microstates (Kondepudi and Prigogine, 1998). Returning to the context of communication theory, maximum entropy is obtained during the transmission of a message of a length n when an alphabet with the largest number of symbols is employed, and the relative occurrence frequency of each symbol is identical.

To characterize the emergence and evolution of transport self-organization in a computational field as the dissolution-precipitation reactive processes in the field advance, we adopt a straightforward use of the Shannon entropy, in a similar vein to Zehe et

al (2021) and Shavelzon and Edery (2024), where it was employed in the context of characterizing self-organization in non-reactive flow in a heterogeneous porous medium. We calculate the Shannon entropy of particle distribution in the direction transverse to flow at a dimensionless time $\tilde{t}$ as a function of distance from the inlet x, $S(x,\tilde{t})$, using the same formula as in (1), reprinted here as

$$S(x,\tilde{t}) = -\Sigma_i p_i \log_2 p_i \tag{2}$$

where $p_i = N_i/N_{tot},\ i = 1...N_y$ is the relative concentration distribution at $x,\tilde{t}$ in the direction transverse to flow (here, N_i is the current number of particles of a specific specie in the i-th cell in the vertical direction at x and N_{tot} is the total number of particles of that specie in all cells at x, taken at a dimensionless time $\tilde{t}$). This quantity has an upper bound of $S_{max} = \log_2 N_y$, corresponding to the state of maximum entropy, or homogeneity of transport in the field, where the same number of particles has visited each of the N_y computational cells at a given distance from inlet x; the obvious lower bound of 0 corresponds to the state of maximum transport spatial organization in the field, namely all particles follow a single preferential flow path (Zehe et al (2021) and Shavelzon and Edery (2024)).

References:

- Shavelzon and Edery (2024), Shannon entropy of transport self-organization due to dissolution–precipitation reaction at varying Peclet numbers in initially homogeneous porous media.
- Shannon (1948), A Mathematical Theory Of Communication.
- Zehe et al (2021), Preferential Pathways for Fluid and Solutes in Heterogeneous Groundwater Systems.
- Edery and Stolar (2021), Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields.
- Edery et al (2011), Dissolution and precipitation dynamics during dedolomitization.
- Singurindy and Berkowitz (2003), Flow, dissolution, and precipitation in dolomite.
- Al-Khulaifi et al(2017), Reaction Rates in Chemically Heterogeneous Rock: Coupled Impact of Structure and Flow Properties Studied by X-ray Microtomography
- Manahan (2000), Environmental Chemistry (9th edn).
- Amorsson (1981), Mineral Deposition From Icelandic Geothermal Waters: Environmental and Utilization Problems.
- Snaebjornsdottir et al (2020), Carbon dioxide storage through mineral carbonation.
- Ruprecht and Falta (2012), COMPARISON OF SUPERCRITICAL AND DISSOLVED CO2 INJECTION SCHEMES.

- Pradhan et al (2025), Determination of CO2 solubility in brines and produced waters of various salinities for CO2 EOR and storage applications.
- Ahmad et al (2016), Injection of CO2-saturated brine in geological reservoir: A way to enhanced storage safety.
- Oldenburg et al (2001), Carbon Sequestration with Enhanced Gas Recovery: Identifying Candidate Sites for Pilot Study.
- Cao et al (2013), Dynamic alterations in wellbore cement integrity due to geochemical reactions in CO2-rich environments.
- Haugen et al (2023), Multi-scale dissolution dynamics for carbon sequestration in carbonate rock samples.
- Harrison et al (2015), The impact of evolving mineral–water–gas interfacial areas on mineral–fluid reaction rates in unsaturated porous media.
- Deutsch (1997), GSLIB Geostatistical Software Library and User's Guide.
- Morse and Mackenzie (1990), Geochemistry of Sedimentary Carbonates
- Kreft and Zuber (1978), On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions.
- Perez et al (2019), Reactive Random Walk Particle Tracking and Its Equivalence With the Advection-Diffusion-Reaction Equation.
- Risken (1996), The Fokker-Planck Equation: Methods of Solution and Applications.
- Press et al (1992), Numerical Recipes in C: The Art of Scientific Computing.
- Kloeden (1992), Numerical solution of stochastic differential equations.
- Domenico and Schwartz, Physical and Chemical Hydrogeology, 2nd Edition.
- Le Borgne et al (2008), Lagrangian Statistical Model for Transport in Highly Heterogeneous Velocity Fields.
- Gudagninin and Neumann (1999), Nonlocal and localized analyses of conditional mean steady state flow in bounded, randomly nonuniform domains: 1. Theory and computational approach.