Reply to comments on EGUSPHERE-2025-381

RC1: 'Comment on egusphere-2025-381', Anonymous Referee #1, 9th June 2025

Citation: (https://doi.org/10.5194/egusphere-2025-381-RC1)

Suitner and colleagues tackle the important question of runaway precipitation as a potential effect of ocean alkalinity enhancement. They use experimental data to derive logistic functions to describe the progression and identify distinct phases of the runaway precipitation process. The aragonite saturation state and available nucleation surface area are identified as key drivers behind the precipitation process. The authors conclude by speculating about the impact of particle removal through sinking on the possible magnitude of runaway precipitation in natural systems.

While the authors present interesting data, I struggle to see how the study advances our understanding of runaway precipitation. My main criticism is that the logistic function presented as a conceptual model is not generalised and anchored to critical environmental factors. The coefficients for the functions are derived from each experimental dataset and are thereby not generalisable (which the authors acknowledge). No attempt is made to describe how the aragonite saturation state and available surface area for precipitation impact the coefficients of the logistic function, despite these factors being identified as key drivers behind the precipitation process in this very study. The equation also does not account for temperature, salinity, or the concentrations of known precipitation inhibitors. As such, the suggested logistic models have no predictive power outside of the specific experimental conditions from which they were extracted. I would encourage the authors to reassess their data and possibly conduct follow-up experiments to mathematically describe critical environmental and chemical factors, which would result in a true conceptual model. That runaway precipitation follows a logistic function was already concluded by Suitner et al. (2024), so I do not see this manuscript as a substantially novel contribution.

Thank you very much for your feedback. We appreciate the level of detail in your comments. You will find a point-by-point response to each comment below.

Reply to the general comment:

The initial idea of this work was to refine the analysis of the existing experimental datasets from Suitner et al. (2024), as major aspects, like the rate equations or a thorough description of main drivers of the precipitation process, have not been discussed in detail. Said so, we agree with the reviewer that the next fundamental step would be the implementation of critical environmental factors (e.g. temperature, salinity, sediment load, inhibitors, etc.) into the provided equations. We anticipate that a whole series of experiments aiming to achieve this goal are ongoing or planned within the next years. We agree that a single setup is insufficient to generalize the described functions and patterns. Therefore, more settings with varying environmental factors should be and are currently being investigated. Nevertheless, the existing data also appear to provide sufficient indications for developing generalizable descriptions of overall patterns. L297-298: "For the present study, the compiled concepts allowed the description of the principles guiding the entire runaway process in site-specific condition". The general "shape" and the key drivers of the process have been identified and cross-connections pointed out.

The logistic function is thereby employed as a suitable fit to describe the "shape" of the TA loss/precipitation process by transforming discrete data series into continuous functions. It was not intended to expand the related curve fits into an overarching predictive model. For the present setup, the characterized continuous functions combined with the classical rate equations seem to outline the measured data quite well.

L298-303: "The obtained capability to predict TA-stability ranges, in terms of time and magnitude, might help preventing secondary mineral formation, thereby optimizing the assessments for OAE

application scenarios. Furthermore, the simplicity of the logistic curve fit model, along with the demonstration that the carbonate precipitation follows simple rate law equations “[…], might facilitate the straightforward integration of these fundamental mechanisms into ocean models […]”
A future potential predictive model might therefore be derived from rate equations, with substituted logistic curve-fits for the evolution of Ω_{ar} and/or the particle surface area. Environmental factors would typically modify the rate equation rather than the logistic curve fit of carbonate chemistry parameters.

The methodology is only described very briefly and relies heavily on citations of previous work. Even if a full repetition of methods is not needed, a more extensive description is required in the current manuscript to explain the limits and results of the study.

It was a deliberate decision to cut the method section, as this work is almost entirely theoretical. We acknowledge the reviewer’s request, and an additional chapter describing the methodology of the data acquisition studies will be added to improve clarity. We would like to suggest to provide a short overview in the main text, while providing a more detailed version in the supplements as well.

Finally, I encourage the authors to publish the data either as a supplement to the manuscript or as a separate dataset.

All datasets will be made fully accessible during/after the publication process. Either via Biogeosciences or through a data repository like PANGAEA or Zenodo.

Minor comments:

TA and alkalinity are used interchangeably throughout the text; be consistent.

For consistency, total alkalinity will be referred to as TA throughout the entire text. Thanks for noticing.

L46-48: I am sure this is not the authors’ intention, but to me, the sentence suggests that NETs can be seen as an alternative to emission reductions. Consider rephrasing.

It will be rephrased accordingly:

[New]:
“To mitigate climate change and reach net-zero greenhouse gas emissions by the end of the century, negative emission technologies (NETs) are necessary **besides greenhouse gas emission reduction** (UNFCCC, 2015) considering the slow change in the development of the energy infrastructure, lifestyle of humanity, and national goals for economic growth (Fuss et al., 2018; Iyer et al., 2015; Sers & Victor, 2018).”

[Old]:
“To mitigate climate change and reach net-zero greenhouse gas emissions by the end of the century, negative emission technologies (NETs) are necessary (UNFCCC, 2015) considering the slow change in the development of the energy infrastructure, lifestyle of humanity, and national goals for economic growth (Fuss et al., 2018; Iyer et al., 2015; Sers & Victor, 2018).”

L91: Here, it seems like runaway precipitation is a desired phenomenon. Consider rephrasing.

Sentence slightly changed to:
[New]:
"To sustain a triggered runaway carbonate formation (Fig. 1), it is necessary to retain the precipitates in the system."

[Old]:
"To sustain the observed runaway carbonate formation (Fig. 1), it is essential to retain the precipitates in the system."

Section 2.1: The description of the experimental setup is too brief; it is not enough to refer to Suitner et al. (2024). Please include information about initial TA concentrations and aragonite saturation states, number of replicates, samples collected, analysis methods and uncertainties, etc. The Gran Canaria setup should also be briefly introduced here, since seemingly new results from that experiment are presented in this manuscript.

Thank you very much for the comment. The description of the experimental setup from the Suitner et al. (2024) study will be expanded and the requested information given. Since only the grain size distribution of the precipitates from the Gran Canaria study is included here, the authors suggest limiting the description of the study to a minimum, approximately 2-3 sentences to provide a brief overview. As suggested above, we would also include a more detailed overview of the methods in the supplementary materials.

L131-132: How was the assumed available active mineral surface area obtained? As described below?

The related methodology is described in L134-142

L136: Filtered or unfiltered seawater?

Seawater was 0.2 µm filtered – this information will be added in L136

L139: The BET surface area is a result, and should preferably include an uncertainty as well.

We thank the reviewer for pointing this out. In the new version, the results from multiple measurement runs and the associated uncertainty will be reported.

Section 3.1: The data from treatments that did not experience runaway precipitation are not presented. Please include at least in the supplementary material. Furthermore, please add a table with the coefficients of the logistic functions to the supplementary material.

A table with the coefficients of the logistic functions and plots including all treatment levels, including plots for those without precipitation, will be provided in the supplements as requested. Please note that no curve fitting was performed for treatment levels without precipitation.

L160-161: The removal of outliers needs to be described in detail here, as the entire manuscript is based on curve fitting. I also suggest including removed data points in Fig. 3 as empty symbols.

Text and plots (Fig. 3 as well as S2 and S3, which might be moved to the main text – see next comment) will be adjusted as suggested.

Figure 3: The filtered neq and filtered eq treatments show quite different patterns from the unfiltered neq treatment, and I think those figures should be shown in the main text.

We thank the reviewer for this suggestion; however, after some discussions, we have decided not to include all three plots in the main text, as it would overload the manuscript and not provide additional insights into the overall process. Displaying these datasets would also necessitate presenting all related tables with coefficients and at least some, if not all, associated conceptual figures (such as those in Fig. 9 and S8). Regarding the filtered neq approach, deviations in the patterns originate from various treatment levels that triggered the APP almost immediately. Consequently, the corresponding diagram would appear overloaded with information, but it would show similar behavior in detail. The differing characteristics of a CO_2-equilibrated approach naturally result in diverging absolute numbers, but the method for determining the logistic function remains the same. Furthermore, both requested diagrams have already been presented in Suitner et al. (2024), and reproducing them would simply replicate results already available there.

Figure 3A-B: I suggest adding the TA concentration and aragonite saturation state of the initial seawater to the figure as well.

We appreciate the suggestion, it will be implemented as recommended.

L192-194: Please include as a figure in the supplementary material.

It will be provided as requested.

L219: Confusing phrasing, there is a decrease in APP timespan with increasing initial TA.

Thank you very much for noticing. This will be rephrased to:

[New]:
"In the eq approach, the APPs showed a continuous decrease as the initial TA addition levels increased, ranging from 5 to 11 days."

[Old]:
"APPs in the eq approach showed a continuous increase ranging from 5 to 11 days."

Section 3.4: I find this section somewhat confusing. The coefficients b and c determine the shape of the logistic function, so it is only natural that they correlate well with the induction time and APP timespan (which are determined from the shape of the logistic function).

The idea of this section is to provide simple equations for the conversion of abstract coefficients to relatable parameters. The high correlation is therefore a natural consequence, as pointed out by Referee #1. A sentence will be added in Section 3.4 to clarify this point.

Section 3.5: The manuscript is generally well written; however, I struggled with this section. Please go over the text again.

We would like to suggest the following changes in L232-244:

[New]:

"Additional insights into the reaction speed and the associated timespan of the APP can be obtained through analysis of empirical rate law equations. As an example, Fig. 7 illustrates the relationship between the logarithm of TA-loss rates normalized to the surface area and the aragonite saturation states for the unfiltered neq approach (see Figs. S4 and S5 for details on the filtered approaches), focusing on treatments that entered the APP. Throughout all experiments the logarithm of the surface area normalized TA-loss rates R correlates with the log(Ω_{ar}-1), in accordance with similar observations reported in literature (e.g. Morse et al., 2007; Mucci & Morse, 1983; Zhong & Mucci, 1989). The parameters n and k in Eq (2): $R = k(\Omega_{ar}-1)^n$ were determined for each treatment level in this work, as outlined in Eq (2) to (4) (section 2.3). Here, R represents the surface area normalized TA-loss rate, and k denotes the rate constant.

The values for n and log(k) derived from the linear regressions in the unfiltered neq treatments are provided in Tab. 3 (see Tab. S1 and S2 for filtered experiments). These values demonstrate reasonable consistency in n and log(k) within each of the three separate experiments. Treatment levels influenced by the immediate formation of $Mg(OH)_2$ as pH approached approximately 10.3 show minor deviations, the remaining treatment levels exhibit reaction orders (n) within a relatively narrow range of 2.45 to 2.73. In comparison, log(k) values ranged between 0.30-1.68, showcasing a higher variability."

[Old]:

"Further implications about the reaction speed and the related timespan of the APP can be provided by empirical rate law equations. As an example, Fig. 7 demonstrates the relationship between the logarithm of TA-loss rates normalized by surface area and aragonite saturation states for the unfiltered neq approach (see Fig. S4 and S5 for details on filtered approaches), for treatments that entered the accelerated precipitation phase. Throughout all experiments log(R) TA-loss rates correlate with the log(Ωar-1), expressing the characteristic relationship for carbonate formation (see Morse et al., 2007; Mucci & Morse, 1983; Zhong & Mucci, 1989). The strong correlation of the linear regressions within each experiment enables the articulation of the empirical rate equations, such as Eq. (2): $R = k(\Omega_{ar}\text{-}1)^n$. In this equation R represents the surface area normalized TA-loss rate, k the rate constant and n the reaction order. The related values for n and log(k) derived from the linear regressions are provided in Tab. 3 (see Tab. S1 and S2 for filtered experiments), showing reasonable consistency in n and log(k) values within each of the three separate experiments. While some treatments, showing immediate Mg(OH)2 formation, slightly deviate, the other treatment levels displayed reaction orders (n) within a relatively narrow range of 2.45 to 2.73. In comparison, log(k) values ranged between 0.30-1.68, showcasing a higher variability."

Section 3.6: Here, it would be interesting to compare n and k between treatments, so I think it would be relevant to show data for filtered neq and filtered eq as additional panels in Figure 7 and Table 3.

Thank you very much for the suggestion. So far, the data for filtered setups are just presented in the supplements, and the main body of the text is consequently only showing the unfiltered treatments, assumed to be the closest to natural seawater conditions. As already stated above, we generally decided against overloading the main body of the text.

Expanding figure 7 to 3 panels would generally be possible, if required, but would also reduce its readability. The same applies to a related overview table for n and k values.
To nevertheless provide an option for a cross-treatment comparison, we would like to suggest providing the suggested overview figure and table in the supplements, while referring to them in the main text. We are open for all suggested options.

L242: Please specify what is meant by "some treatments".

We will make it explicit in the new version of the manuscript.

L279: What is meant by "in dependence to a variable density"?

Since the density for each individual particle is unknown, a range of densities was assumed to estimate a realistic range for sinking velocities (shown as the gray range, centered in Fig. 8). Also see the reply for the next comment.

L271-285: I found it hard to follow this paragraph and to understand when particles observed by SEM, particles measured by FlowCam, and purely calculated values are referred to.

This section was reworked as:

[New]:
The gravitational sinking velocities of precipitated particles were measured using a FlowCam setup (see Bach et al.,2012 for technical details). Based on the concept of equivalent spherical diameters (ESD) the density of each particle was calculated, revealing a range from 1.54 to 3.18 g cm^{-3} for ESD sizes between 12 and 50 µm. The average density was determined to be 2.358 g cm^{-3}. The discrepancy with the density of aragonite (~2.95 g cm^{-3}) may result from an overestimation of particle sizes in the calculation method, which relies on an inversion of Stokes' Law for the terminal sinking velocity of perfect spheres. However, most particles are non-spherical and contain numerous internal cavities within their structure (see Fig. S1), and their densities are therefore expected to be lower than those of pure aragonite. The determined particle density was then used to calculate the theoretical sinking velocities of the manually counted precipitated particles. To account for potential variability in particle density, Fig. 8 presents a range of sinking velocities of the counted precipitates.
Measured sinking velocities for precipitated particles within the aforementioned density range varied from ~5 m d^{-1} (14 µm particle) to ~47 m d^{-1} (41 µm particle). Recorded particles in the ESD range of 50-180 µm were not included in the calculations, as they were not observed within the same filter material that was analyzed by visual inspection. Discrepancies between measured and calculated values may reflect aggregation effects or technical limitations of the utilized FlowCam to track particles smaller than 3 µm (Bach et al., 2012).

[Old]:
Based on the distributions of equivalent spherical diameters (ESD), the sinking velocities of the precipitated materials were calculated to identify their hypothetical sinking velocities. To facilitate this calculation, the densities of the aragonite precipitates were determined by actual sinking velocity measurements of the same materials, providing densities of 1.54 to 3.18 g cm^{-3} in an ESD range of 12-50 µm. The discrepancy with the density of aragonite (~2.95 g cm^{-3}) may result from an overestimation of particle sizes in the calculation method, which relies on an inversion of Stokes' Law for the terminal sinking velocity of perfect spheres. However, most particles are not spherical and contain numerous cavities within their structure, which likely contributes to an underestimation of particle densities.

Therefore, Fig. 8 features a range of sinking velocities of the counted precipitates in dependence to a variable density, supported by ESD distributions and ranges for different types of precipitated particles. Measured sinking velocities for precipitated particles within the aforementioned density range varied from ~5 m d^{-1} (14 µm particle) to ~47 m d^{-1} (41 µm particle). Recorded particles in the ESD range of 50-180 µm were not included in the calculations, as they were not observed within the same filter material that was analyzed by visual inspection, yielding densities of 1.1-1.3 g cm^{-3}. Discrepancies between measured and calculated values may reflect aggregation effects for very high values and the technical limitations of the utilized FlowCam to track particles smaller than 3 µm (Bach et al., 2012).

Figure 8: This figure is very busy and should be split up into multiple panels. The particle size distributions should be presented on their own with a clear x-axis. The y-axis is not easily understandable (does it represent both depth and sinking velocity, or depth divided by sinking velocity?), and I do not see what it is related to. Finally, the aragonite density is three orders of magnitude too high.

The authors agree that the density of the information presented is somewhat overwhelming as multiple aspects are shown, 1. sinking velocities, 2. particle size distributions and 3. residence times. Plotting the information in one figure allows the datasets to communicate with each other, as their information is complementary. To enhance readability, we will follow your suggestion and move the particle size distribution to a separate panel. Another y-axis to divide depth and sinking velocity will be added as well. The unit for densities will be corrected, thanks a lot for noticing.

Section 4.1: As I outlined in my main comment, the current model is not predictable, except within the same environmental conditions. Since the model is not actually linked to environmental conditions, it will also not be possible to implement it in ocean models.

We agree that the presented concepts are not generally applicable. L297-298: "For the present study, the compiled concepts allowed the description of the principles guiding the entire runaway process in site-specific condition". We agree that the presented concepts should be enhanced by a functional term for temperature, salinity, and particle density. With ongoing and future experiments, we are aiming to implement variable environmental conditions. Since this is part of a multi-year project, with each experiment lasting approximately three months, additional time is needed to collect the data density required for such a parameterization.

L316: Whitings are precipitation events, not a cause of precipitation.

Wording will be adjusted.

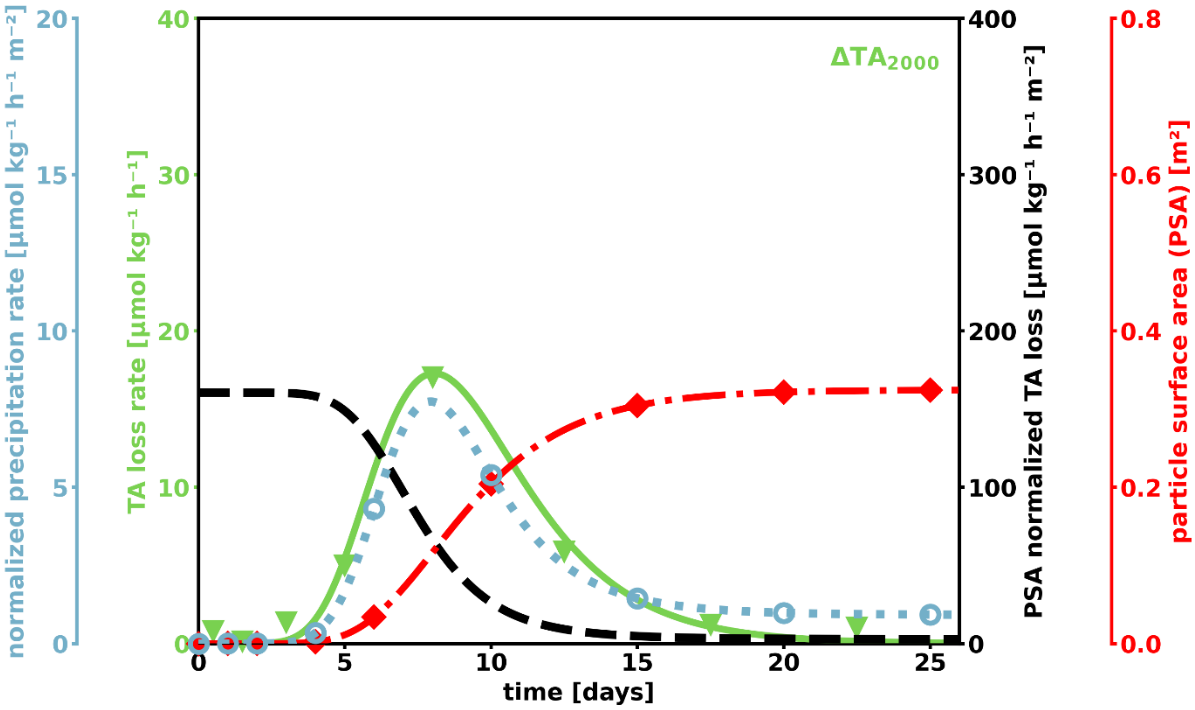
L392: "section", not "chapter".

This will be adjusted.

L399-400: Yes, and this should be reflected in the logistic equations.

Related sentence L399-400: "The interplay of precipitation potential by Ω_{ar} and the practical available surface area could therefore be determined as the primary factors guiding the actual observed TA-loss rates."
Thank you for the comment. Based on your suggestion the calculations for Fig. 9 and S8 were refined. For each panel a new graph was added, which represents the empirical rate equation [$r = k\,A\,(\Omega_{ar}-1)^n$]

including the determined values for n and k; a continuous function for the surface area A (derived from the curve-fitted logistic TA-loss function) and another continuous curve-fitted logistic function for Ω_{ar}. All these parameters combined provide an estimate of the realized aragonite precipitation rate (blue dotted graph). Here is an example plot for ΔTA_{2000}. Hollow blue markers thereby represent the rate equation with the original Ω_{ar} values.



Additionally, the mentioned continuous surface area function (red - dash-dotted graph) replaced the previously reported raw surface area values, which are still given by the red diamonds. The shown diagram represents an example plot as a replacement for the ΔTA_{2000} panel in Fig. S8 (which will be labeled (a)-(f)). All other diagrams of the same type will be adjusted accordingly (Fig. 9 and remaining panels in Fig. S8)

L402-406: But k and n were derived from experiments in natural seawater, containing inhibitors, and based on the experimentally determined saturation state of aragonite (which is then used for the calculation of R). As such, these constants should include the potential impact of inhibitors. Is it not more likely that issues with accurately determining PSA are causing the difference?

L402-406: "For comparison, the blue data points in Fig. 9 represent the calculated theoretical loss rates at each sampling day, by inserting the experimentally determined Ωar and PSA values into the related empirical rate equation for ΔTA2000 (see Tab. 3). As this equation does not account for any inhibitory factors, the resulting rates exhibit a slight positive bias compared to the observed values."
With the new plotting approach (see above), the described effect will be less obvious visually. The text will nevertheless be adjusted accordingly, including a statement for the possible influence of PSA.

L430-434: Again, this shows that temperature and salinity need to be considered in the logistic equation.

L430-434: "Significantly shorter induction times were identified for subtropical conditions (Temp. ~23°C, Sal. ~36 psu, TA ~2400 µmol kg^{-1}). Hartmann et al. (2023) described an onset of the precipitation after just 4 days for a 50µm filtered neq incubation with initial values of 1050 µmol kg^{-1} for ΔTA and ~15 for Ω_{ar}."

We appreciate the suggestion. To our knowledge, all attempts to incorporate terms for temperature and/or salinity to reliably describe carbonate precipitation in natural seawater have so far not been successful. As a result, we are currently conducting new sets of experiments on Gran Canaria to obtain the data necessary to extend the function with temperature sensitivity. Through the ongoing and planned future experiments, we will aim to derive such an equation, considering the diverse environmental parameters that influence precipitation behavior (also see reply to the general comment above).