Response file of He et al., 2025 Biogeosciences

Dear Mr He, Prof Cui,

Apologies for the delay in making this decision while I currently work overseas as well as the delays in finding a second reviewer.

RE: We truly understand the difficulty of securing suitable reviewers and sincerely appreciate your effort in processing this paper under current circumstance.

Thanks for the responses to the constructive feedback that we received from two reviewers. I understand that both reviewers prefer the manuscript to be split into two separate papers. I understand the reasons for this suggestion and appreciate that you agree with their recommendations. I agree that focusing in this manuscript on the RPO aspects would be more suitable and it is great that you will be able to publish the other part of this study separately. Thanks also for your detailed responses, which provide me with a very good overview of structure and content the revised version. Therefore, I invite you to resubmit the revised manuscript, in line with reviewer comments and your responses.

RE: We completely agree that this manuscript would be better after being split into two separate papers. Accordingly, we have reorganized this paper to mainly focus on the suitable pretreatment approaches for ramped-temperature pyrolysis/oxidation (RPO) analysis. While acknowledging a lot of revisions are required, we have extensively rewritten the manuscript and carefully addressed all concerns raised by two reviewers. To improve the overall quality of this manuscript, we have made the following major changes, as outlined below.

First, we have changed the title of this manuscript to "**Technical note: Assessing pretreatment approaches for serial pyrolysis-oxidation analysis of sedimentary organic carbon**".

Second, we have rewritten the Abstract, Introduction, and Conclusions sections. The discussion regarding bulk carbon results has been removed while relevant tables and data have been moved to the supplementary file.

Third, to improve the flow of the manuscript, we have simplified the names of samples and pretreatment approaches according to reviewers' suggestions. More details about RPO

instrument have been provided in the main text and the supplementary file to facilitate the readers' understanding of this key method.

We sincerely thank the Associate Editor for the careful evaluation and the opportunity to resubmit our manuscript. We believe the overall quality of the paper has been significantly improved after revisions.

Thank you and looking forward to your revised manuscript.

RE: We have addressed all the concerns from two reviewers with point-to-point responses below. We sincerely appreciate the opportunity to resubmit our revised manuscript.

Overall response to Reviewer #1's comments:

We sincerely appreciate your valuable comments which substantially improve the quality of our revised MS. After carefully considering your and Reviewer#2's suggestions, we decided to split this MS to 2 papers. The revised MS mainly focuses on the optimal acid pretreatment conditions for ramped-temperature pyrolysis/oxidation (RPO) analysis. Accordingly, some of the suggested changes concerning the sections or statements of bulk OC and $\delta^{13}C$ would not appear in this revised version, but will be incorporated in a second paper specifically on acidification protocols for bulk measurements. In response, we have made extensive revisions to address all the concerns as listed below.

(1) First, we have highlighted the ramped-temperature pyrolysis/oxidation technique and strengthened its connection to acid pretreatment. The introduction section has been reorganized to comprehensively illustrate the methodological impacts on RPO results caused by different acid pretreatments. The title of this manuscript has been changed to "**Technical note: Assessing pretreatment approaches for serial pyrolysis-oxidation analysis of sedimentary organic carbon**". Detailed discussion regarding bulk OC and $\delta^{13}C$ has been removed to streamline this manuscript and to highlight the pretreatment for RPO as the primary focus of this study. Additionally, the schematic of RPO instrument has been added in the supplementary file for readers to get a quick understanding of this technique.

(2) Second, we have carefully improved the overall quality of the manuscript by reorganizing and rewriting. We extensively rewrote the Abstract, Introduction, and Conclusions sections to emphasize the main focus of this study is the optimal acid pretreatment for RPO analysis. The overall length of this manuscript has been significantly reduced by removing the introduction and discussion on bulk OC and $\delta^{13}C$ measurements as well as moving Table 1 and 2 into the supplementary file. Language and clarity throughout the manuscript have been significantly improved through careful editing. The complex sample IDs and method codes have been thoroughly rephrased to more accurate and direct expressions.

We believe these revisions would adequately address reviewers' comments while preserving and highlighting the merits of our work. Now this manuscript presents more clarified and well-organized version with coherent narrative throughout. We are grateful for your thorough suggestions and for considering this manuscript for publication in Biogeosciences.

This article discusses various methods of acidification of sediment samples to remove carbonates and the effects of these acidification methods on the residual organic carbon. The range of acidification methods used are liquid acid of various acid concentrations (hot or room temp, various time intervals) followed by rinsing, fumigation with strong acid followed either no rinse or rinse and the dried by either oven drying or freeze drying. They then evaluate the remaining carbon by total carbon measurements

and stable carbon measurements. They then discuss a relatively new ramped temperature pyrolysis/oxidation (RPO) technique where they test the various acidified samples by heating and provide data and interpretation of CO2 evolution versus temperature.

The information in the paper is worthy of publication. But significant editorial changes and clarifications are needed. I include a scan of the MS with rough suggestions/comments.

RE: Thank you for your positive feedbacks and detailed examination. We have carefully addressed your comments and concerns to enhance the readability and clarity of this manuscript. Now this manuscript highlights the optimal pretreatment protocols for RPO analysis.

General comments

My most major comment is that it seems that this MS could be broken into two different papers. One with the acidification portion and TOC and d13C study. One with the RPO study. The two parts of the paper are not well joined. The conclusion section is nearly all (or all but the last sentence) about the acidification portion.

RE: Thank you for your insightful comment. We fully agree with you that two parts of this paper are not well joined and the focus of conclusion section is not well-balanced. This study was originally designed to test how different acidification conditions impact the organic geochemical results of sedimentary organic carbon. To investigate this, bulk measurements and RPO analysis were selected as two different but complementary analyses. As reviewers pointed out, the linkage is not very clearly illustrated and the paper is too long for readers to follow throughout.

Accordingly, to enhance the clarity and readability of this paper, we decided to split this MS into 2 papers according to both reviewers' suggestions. This revised MS will primarily focus on the assessment of pretreatments on RPO results. We will potentially submit a second paper later in time, after carrying out some new work as suggested by Reviewer #2.

For this current revised manuscript, we:

(1) Removed the discussion on the bulk results (Section 3.1) and mainly focused on the RPO part.
(2) Revised Table 1 to only include major variables in the MS. Other minor variables have been moved to the supplementary file to complement our overall conclusions.
(3) Moved the second Table (Table 2) to the supplementary file as bulk parameters are no longer the focus of this paper.
(4) Shortened/Revised the Abstract, Introduction and Conclusions to highlight our RPO results.
(5) Moved methodological details of $CaCl_2$ addition experiment to the Method part to

streamline the Discussion section.

Much of the language throughout needs cleaning up. Examples of odd word choices and potential changes:

RE: We have carefully read all your line comments and reworded our sentences according to your suggestions. We would like to clarify that some paragraphs/sentences have been removed during major revision and restructuring of the main text. We sincerely appreciate your detailed suggestions, which substantially improved the MS. Please see the detailed replies below.

"more proximal to pristine" – "more similar to pristine"

RE: Now has been corrected in line 34.

"strikingly discrepant" – "Strikingly different"

RE: This sentence has been removed in the revised manuscript.

"Current instrument advancing allows" - "Current instruments allows"

RE: This phrase has been reorganized to introduce the applications of the RPO technique.

"superposition of myriad signals" - "addition of several signals"

RE: This sentence has been rephrased in line 47 as *"RPO technique has emerged as a transformative approach that interprets organic carbon (OC) as a thermal reactivity continuum, effectively deconvolving bulk signatures into component fractions"* to compare two analytical tools.

"we carefully instilled several drops" - "we carefully added several drops"

RE: Revised as suggested in line 152.

"13C-enriched moieties" – Maybe "13C-enriched compounds"

RE: The original statement has been eliminated in this manuscript. This point can be better addressed in another paper regarding what is lost during acidification.

"To reconcile and depict coincident" – "To illustrate"?

RE: Now has changed to "To explicitly illustrate" in line 311.

"exhibit constant gradation" ?

RE: Now has been corrected to "exhibit consistent thermographic shift" in line 391. Similarly, "systematic gradation" has been corrected to "systematic shifts" throughout the main text.

"Besides, our study" - "Finally, our study"

RE: Now has been revised to “Overall, …” in line 499.

Specific comments below - see also the scan MS with handwritten comments

RE: We are grateful to your thorough examination and constructive comments. Your handwritten comments have been organized into points listed at the end of this part. Please find our point-to-point replies here as well as in our revised MS.

Four samples are used for the various treatments. Each of the samples is abbreviated but the abbreviates are far too complex. For example, one sedimentary rock is abbreviated “1207-GR-11”. Another sedimentary rock is “MS05-135”. Why not just call them Sed1 and Sed2. No need for complex abbreviation that confuses the reader and makes the reader must refer back each time the sample is named.

RE: Thank you for your detailed comments concerning the clarity of sample abbreviations. Accordingly, we renamed the two sedimentary rocks as “SR1” and “SR2”, and the two modern sediments as “Sed1” and “Sed2”, respectively. “1207-GR-11” - “SR1”, “MS05-135” - “SR2”, “CJK A6-3” - “Sed1”, “AREX R7” - “Sed2”. Sample names in our main text and figure legends are correspondingly abbreviated.

In section 2.2 the different acidification methods are termed EC1 through EC12. Define EC – it might be “experimental condition” but the reader is unclear why “EC” is used.

RE: Now has been clarified. Reviewer made a clear point that EC is the abbreviation of “experimental condition”. To avoid confusion, “EC” names have been removed in the main text. In addition, Table 1 has been revised to only include major factors that have been discussed in the main text. More informative legends have been used in revised figures, for example “1 N rinse”, to present different groups with different experimental conditions.

In section 2.2 EC11 and EC12 are also named “fume I” and “fume II” – this is confusing.

RE: Thank you for your feedback. In the original we used “fume I” and “fume II” to emphasize that they are two different methods (We cannot apply this to acid rinsed samples as there are too many groups). Nonetheless, we agree with you that it is confusing and unfriendly for the readers. To address this, the expressions are revised to more informative forms (e.g., fumigation-rinse method) throughout the MS.

Table 1 needs work. What is “Mark*”. Maybe add an additional column that shows that EC-1 is the control. And that EC11 and EC12 are also named “fume I” and “fume II”

RE: “Mark*” has been changed to “Abbreviation*” in Table 1. The complete form of Table 1 has been moved to supplementary file as Table S1. To remind the readers that 1 N acid rinse group is the control, we append information to the bottom of Table 1. For “fume I” and “fume

II" expression, we replaced them with more direct names——fumigation and fumigation-rinsing.

Line 104 - Air drying – the reviewer thinks that this is room temperature drying. "Oven drying" is also air drying. Need clarification.

RE: As suggested, the phrase "at room temperature" has been added after "Air drying" in line 162 as suggested.

Line 107 – This is a reviewer's pet peeve. "… to remove acid vapors completely" – Oven drying or freeze drying of fumigated samples might remove acid vapors but any acid vapors that settled on the sample remain. In fact, as water is evaporated remaining HCl simply becomes more concentrated until no more water can evaporate. The HCl remains on the sample and in the silver capsule. Just a note.

RE: we apologize for misleading narrative. We revised the paragraph, as:

"Fumigated subsamples were dried at 60 ℃ given that low temperature is inefficient in removing water vapor since the fumigated subsamples is prone to moisture absorption."

Table 2. Carbonate % needs work. First, what is this carbonate? In the original sample? In the acidified sample (hard to believe – if this much carbonate remained in the sample post acidification, then EC1 through EC11 all completely fail)? How was it measured? No mention of method. What are some N.A. Is EC12 the only method that removed all carbonate or is it the only method that carbonate was not measured?

RE: Thank you for pointing out this underlying problem. Carbonate% is the weight percentage of mass loss in the original samples. The calculation of Carbonate% is based on the mass of sediments lost during aqueous acidification. This definition is inappropriate for acid fumigation method due to the remaining $CaCl_2$.

In the revised paper, the original Table 2 has been moved to supplementary file as Table S2. To avoid confusion, "Carbonate%" in Table S2 has been changed to "Mass loss%" with a brief explanation of it.

Section 4 RPO. In general, RPO should be spelled out a few more times. Maybe at the start of the various sections.

RE: RPO has now been spelled out at its first appearance in each section.

A drawing of the RPO system would be great. It would help to understand the upper and lower sections.

RE: Thank you. As suggested, we added a RPO instrument schematic in our supplementary file. One can also refer to Rosenheim et al. (2008) and Hemingway et al. (2017) for the schematic

of RPO instrument.

Are the RPO catalytic wires designed to be consumables and replace often? What material?

RE: The RPO catalytic wires are consumables and composed of several strands of thin copper wires, nickel wires, and platinum wires entangling together. The oxidation efficiency of catalytic wires is periodically monitored by analyzing an in-house standard (Irati T2 Shale). The catalytic wires are replaced every a few months. However, samples containing considerable Cl (e.g., treated by acid fumigation) may corrode and melt the catalytic wires, as mentioned in the main text and shown in the supplementary file.

Line 134 "whereas" is the wrong word.

RE: The word "whereas" has been deleted.

Figure 1 – the names for the various treatments on the x-axes are confusing. They are not the "EC" names. They should be consistent. Also they are not in the same numerical order as the "EC" names.

RE: We fully agree that using different expressions is confusing. For consistence, the names in all figures and main text have been revised to more informative forms. Figure 1 has been removed since the focus of this paper has now been changed to the impacts of acidification methods on RPO results according to your and R2's suggestions. The bulk parameters and other relevant analyses of the residual sediments and the supernatant can be expanded into another comprehensive study in the future.

Again, using both "EC12" and "fume II" is confusing

RE: The inconsistent expressions have been replaced by using direct descriptions like fumigation method throughout the MS. In the following part, your handwritten comments in the scan MS have been organized by order and responded correspondingly.

<u>the scan MS with handwritten comments</u>

Abstract

p1, L7.

RE: This sentence has been rephrased to illustrate acidification is primarily adopted prior to RPO analysis, as: *"While acid pretreatment is routinely employed to remove carbonates prior to RPO analysis, its methodological impacts remain poorly constrained compared to other geochemical measurements (e.g., $\delta^{13}C$)."* in line 12.

p1, L8.

RE: This sentence has been eliminated in the revised MS as the main focus is on decarbonation pretreatment for RPO analysis.

p1, L9-10.

RE: This sentence has been rephrased to *"We demonstrate that both acidification method (rinsing vs. fumigation) and HCl concentration significantly affect RPO thermograms, with observed differences attributed to the alteration of organic-inorganic associations and selective leaching of acid-soluble OC."* in line 29.

p1, L13.

RE: The discussion on bulk parameters and relevant points has been eliminated in this current manuscript and will be expanded to another follow-up paper on acidification methods.

p1, L18.

RE: Now has been rephrased to *"We demonstrate that both acidification method (rinsing vs. fumigation) and HCl concentration significantly affect RPO thermograms, with observed differences attributed to the alteration of organic-inorganic associations and selective leaching of acid-soluble OC."* in line 29.

p1, L19.

RE: Changed to "*... are more similar to the raw material*" in line 34.

p1, L20.

RE: Done.

"No mention of isotopes".

RE: This paragraph has been revised to align better with the objectives of the revised paper. We appreciate this merit. However, as the focus of this paper is mainly on acidification and RPO, detailed discussion of TOC and isotopes has been removed from the main text. Thus, we do not incorporate too much content regarding isotopes in the abstract and other sections. Nonetheless, the discussion about isotopes and results of other analytical methods is thought to be informative, which can be the main points of another paper in the future.

Introduction

p1, L24, "Maybe $\delta^{13}C_{org}$ throughout".

RE: "$\delta^{13}C$" has been changed to "$\delta^{13}C_{org}$" throughout the MS. This expression in the first paragraph of Introduction has been removed due to the restructuring of the main text.

p2, L30.

RE: Done as suggested. This sentence has been rephrased to introduce applications of RPO in recent studies.

p2, L32.

RE: Done. This sentence has been eliminated due to the restructuring of the Introduction section.

p2, L34.

RE: Done. This sentence has been rephrased to align better with the introduction of RPO analysis.

p2, L36.

RE: "HCl" has been added in line 74.

p2, L37-38.

RE: The expression has been corrected as suggested in 74.

p2, L42, "the temperatures selected for the latter".

RE: We intended to say that higher temperature may lead to greater loss of volatile OC. However, it is ambiguous and is likely not significant enough to be resolvable at the bulk OC level. Therefore, this expression has been removed and "in OC composition" has been added at the end of this sentence to specify the uncertainties outlined here.

p2, L44, "which studies".

RE: The studies were mentioned in the previous paragraph. To avoid confusion, we remove this sentence and provide more detailed discussion about the influence of acidification prior to bulk and RPO measurements in this part.

p2, L45.

RE: This sentence has been removed due to restructuring of the main text. This point has been incorporated in the main text.

p2, L46.

RE: This point "bulk data is the addition of several signals" has been incorporated in the introduction and conclusion section.

p2, L48-49.

RE: The references have been moved to the previous sentence in line 49. At the end of this paragraph in the revised paper, recent applications of RPO analysis have been added to smoothly relate influence of acidification to RPO results. This point (impacts of acidification

on RPO results) has been emphasized in the introduction and other sections to enhance the clarity.

p2, L57-58.

RE: This sentence has been revised in line 110.

Section 2.1

"Why use complex names for samples? Maybe simple names would be easier for readers."

RE: Thank you for suggestions. The abbreviations of four samples have been simplified as SR1&2 and Sed1&2 in the previous RE. Some other information such as "Eocene" has not been emphasized because it is of little use in this study.

Section 2.2

p3, L74.

RE: Done as suggested in the previous RE.

p3, L81, "repeat about?".

RE: Sorry for inattention. This repeated sentence has been deleted.

p3, L87.

RE: Done in line 150.

p3, L90.

RE: Done in line 152.

p4, Table 1.

RE: Fume I and fume II have been replaced with more direct expressions in the MS.

p4, L104.

RE: Done as suggested in line 162.

p4, L107, "HCl will never dry out completely. Water is removed. Remaining HCl will get more concentrated.".

RE: This sentence has been rephrased to avoid confusion in line 166.

Section 2.3

p5, L116.

RE: Corrected in line 182.

p5, Table 2.

RE: The Table 2 has been moved to the supplementary file (Table S2) as the focus of the paper has changed to RPO pretreatments.

Section 2.4

p6, "An image or drawing of RPO system would be useful".

RE: Now has been added in the supplementary file.

p7, L126, "Pt? What type?".

RE: The materials of catalytic wires have been added in line 192.

p7, L134.

RE: Done in line 201.

p7, L136.

RE: This paragraph has been moved to Section 2.5.

Section 2.5

p7, L144.

RE: Corrected as suggested. This sentence has been incorporated into Table 1.

Section 3.1

p8, L174.

RE: This sentence has been eliminated as the discussion about bulk parameters has been removed in the revised paper.

p8, L177.

RE: This sentence has been eliminated as the discussion about bulk parameters has been removed in the revised paper.

p8, L178.

RE: This sentence has been eliminated as the discussion about bulk parameters has been removed in the revised paper.

p9, Fig 1.

RE: This figure has been removed as the focus of this paper is mainly on the RPO pretreatments. Thank you for your comments. All of these suggestions would be considered carefully and likely be incorporated in a second paper focusing on influence of acidification on bulk

parameters.

p9, L196.

RE: This sentence has been removed due to the restructuring of the paper.

p10, L199.

RE: This sentence has been eliminated due to the restructuring of the paper.

p10, L201-203.

RE: This sentence has been eliminated due to the restructuring of the paper.

p10, L205-208.

RE: Thermographic property is actually the RPO result. As RPO is the only thermochemical method adopted in this study, this expression may not lead to additional confusion. Yet, this paragraph has been removed due to the restructuring of the paper.

Section 3.2

RE: We change the title of this section to "**HCl concentration influences on thermochemical properties and potential mechanisms**" as suggested. Note that this section has now become Section 3.1 as the original section 3.1 has been removed.

p10, "spell out RPO at start of new section (remind readers)".

RE: The term ramped-temperature pyrolysis/oxidation has been mentioned and spelt out more times in discussion and conclusions sections to remind the readers. Thank you for your suggestion.

p10, L214.

RE: Done in line 310.

p10, L216.

RE: Done in line 311.

p11, Fig 2.

RE: Arrows have been added in the figure to indicate "orthogonal" variations mentioned in the main text. We use "OC loss" to describe variation in the vertical direction and "chemical alteration" to describe the horizontal shift.

p12, L253-255.

RE: Done as suggested in line 352.

p12, L264.

RE: Done in line 365.

Section 3.3

p13, L285.

RE: Corrected in line 391.

p14, L293.

RE: We didn't add the phrase "in our system" because it is a common phenomenon in a heating system.

Section 3.4

p16, L334.

RE: Done in line 448.

Section 4 Conclusion and recommendations

p17, L349-350.

RE: We revised the whole sentence as: *"We demonstrate that both acid rinsing (particularly acid concentration) and fumigation significantly alter thermochemical properties, with higher acid concentrations promoting mineral dissolution, modifying organo-mineral interaction and leaching soluble OC fractions."* as suggested in line 465.

p17, L358.

RE: We appreciate your suggestion. This point (acidification method for most sediment types) can be the main point in another paper that mainly focuses on the pretreatment protocols for different types of sediments.

p17, L361-362, "odd to bring all these methods up in conclusions".

RE: We agree with your comment. Analytic methods that are not closely related to this study are removed to ensure the focus of this manuscript on RPO pretreatments.

p17, L363-364.

RE: This sentence has been streamlined as *"Freeze-drying remains effective but requires strict contamination control (Jiang et al., 2023)."* for clarity in line 490.

p17, L365-366.

RE: Done as suggested. The sentence has been rephrased as "*While heating accelerates*

decarbonation, it should be avoided for organic-rich (e.g., protein-rich) sediments to prevent hydrolytic OC loss and leaching of soluble OC." in line 492.

p17, L367.

RE: Done as suggested. Thermochemical analysis is RPO here. To clearly relate to the main points of this paper and to emphasize the merit of RPO analysis, the sentence has been rephrased as: *"Overall, this work establishes that RPO, when paired with appropriate sample preparation, can resolve subtle OC properties obscured by bulk analytical approaches."*

All of your suggestions and concerns have been carefully considered and addressed. We are very grateful to you for your time and effort invested in reviewing our MS.

References cited

Rosenheim, B. E., Day, M. B., Domack, E., Schrum, H., Benthien, A., and Hayes, J. M.: Antarctic sediment chronology by programmed-temperature pyrolysis: Methodology and data treatment, Geochemistry, Geophysics, Geosystems, 9, 2008.

Hemingway, J. D., Rothman, D. H., Rosengard, S. Z., and Galy, V. V.: An inverse method to relate organic carbon reactivity to isotope composition from serial oxidation, Biogeosciences, 14, 5099-5114, 2017.

Overall response to Reviewer #2's comments:

We sincerely appreciate your positive feedbacks and constructive suggestions, which significantly improve the overall clarity of this manuscript. After carefully considering your and Reviewer#1's suggestions, we decide to split this MS to 2 separate papers, with the current revised MS mainly focusing on the optimal pretreatment approaches for RPO analysis. Accordingly, some of the suggested changes concerning the sections or statements of bulk OC and $\delta^{13}C$ would not appear in this revised version, but will be incorporated in a second paper specifically on acidification protocols for bulk measurements. In response, we have made extensive revisions to address all the concerns as listed below.

(1) First, we have highlighted the ramped-temperature pyrolysis/oxidation technique and strengthened its connection to acid pretreatment. The introduction section has been reorganized to comprehensively illustrate the methodological impacts on RPO results caused by different acid pretreatments. The title of this manuscript has been changed to "**Technical note: Assessing pretreatment approaches for serial pyrolysis-oxidation analysis of sedimentary organic carbon**". Detailed discussion regarding bulk OC and $\delta^{13}C$ has been removed to streamline this manuscript and to highlight the pretreatment for RPO as the primary focus of this study. Additionally, the schematic of RPO instrument has been added in the supplementary file for readers to get a quick understanding of this technique.

(2) Second, we have carefully improved the overall quality of the manuscript by reorganizing and rewriting. We extensively rewrote the Abstract, Introduction, and Conclusions sections to emphasize the main focus of this study on the optimal acid pretreatment conditions for RPO analysis. The overall length of this manuscript has been significantly reduced by removing the introduction and discussion on bulk OC and $\delta^{13}C$ measurements as well as moving Table 1 and 2 into the supplementary file. Language and clarity throughout the manuscript have been significantly improved through careful editing. The complex sample IDs and method codes have been thoroughly rephrased to more accurate and direct expressions.

We believe these revisions would adequately address reviewers' comments while preserving and highlighting the merits of our work. Now this manuscript presents more clarified and well-organized version with coherent narrative throughout. We are grateful for your thorough suggestions and for considering this manuscript for publication in Biogeosciences.

General comments

I think this is a good study but could do with more information such as C/N, FTIR etc. And I would have liked to see the results of what was lost (since you did talk about the supernant)

RE: Thank you for your positive feedbacks. According to your and R1's comments, we decide

to split the original submission into two papers, with the current revised version focus specifically on how acidification affects RPO results. The rest part, especially bulk data, will be supplemented with additional data (e.g., C/N and FTIR) for the preparation of a second paper on the optimal pretreatment protocols for bulk measurements. Accordingly, we fully agree that other proxies (e.g., C/N and FTIR) can be very informative to reveal what was lost during acidification. As the bulk results are no longer the main content in the current revised MS, we decided to include potential more proxies/measurements in the second paper to better support our bulk measurements. Now this revised manuscript highlights the optimal pretreatment conditions for RPO analysis.

The paper is very long and hard to follow.

RE: Thank you for the general comment concerning the length and clarity of this manuscript. After splitting this manuscript into two separate papers, we substantially revised this manuscript to align better with the objectives of this current study. Specifically, we:

(1) Removed the discussion on the bulk results (Section 3.1) and focused on the RPO part.
(2) Revised Table 1 to only include major variables (Acid fumigation and acid rinsing as well as the HCl concentration for rinsing) in the MS. Other minor variables have been moved to supplementary file to complement our overall conclusions.
(3) Moved the second Table (Table 2) to the supplementary file as bulk parameters are no longer the main focus of this paper.
(4) Shortened/Revised the Abstract, Introduction and Conclusions to highlight our main results.
(5) Moved methodological details of $CaCl_2$ addition experiment to the Method part in order to streamline the Discussion section.

I would suggest reducing and making concise, and bringing the RPO and acid experiment together instead of dealing with them separately that makes it hard to evaluate.

RE: The manuscript has been intensively shortened after being split into two separate papers. Unnecessary expressions have been revised/removed according to your specific comments. The discussion on bulk results has been removed to make the structure more concise. In addition, we emphasize this paper is mainly about impact of acidification methodology on the RPO result to reduce likely misunderstanding.

R1's suggestion of 2 papers seems like a good idea to me. There are good results here but I think the paper itself is confusing and hard to read due to sample codes, jumping back and forward for different methods, and the lack of linkage between the acid/RPO experiments.

RE: We appreciate your and R1's suggestions to separate this MS into 2 papers. Upon careful consideration of your comments, we decided to have this MS focus only on RPO results. The

structure of the paper has been correspondingly reorganized to avoid confusing sample codes and jumping discussions.

Nonetheless, the last part of the discussion and the TOC-based normalization are dependent on the bulk data (i.e., TOC) of each individual sample. Considering this, we provided the bulk data (Table 2, now as Table S2) in the supplementary file.

I have commented on the attached pre-print.

RE: Thank you for your thorough examination and careful comments. We have carefully addressed all your suggestions/concerns. All comments in the attached file have been organized in order and responded in the line comments below.

Line comments

p1, L29, "Not the best wording to use here".

RE: This sentence has been eliminated in the revised MS.

p2, L31-32, "such as - some examples and references needed here.".

RE: This statement has been eliminated in the revised MS. Detailed introduction of examples have been included in the introduction of the revised MS.

p2, L36, "Some studies use EDTA to reduce OC loss.".

RE: We respectfully appreciate your suggestion that some studies use EDTA. However, we have not incorporated this point in the revised MS for a few reasons. First, it is not a common protocol for acidification in most studies and is not within the scope of this paper. Second, EDTA is a widely used chelating agent for metals while its role in stabilizing OC and reducing OC loss at low pH has not been well illustrated. Third, some previous studies found that addition of EDTA can lead to extra loss of fulvic compounds (Jez et al., 2021). Thus, to avoid underlying misinterpretation, we do not include this point in the revised MS.

p2, L36, "Get rid of semi colon here. These are two sentences.".

RE: Now has been revised according to your suggestion in line 76.

p2, L39, "may or can".

RE: "might" is changed to "can" in line 79.

p2, L40, "These references are all quite old. There are recent studies available, https://scholar.google.com/scholar?as_ylo=2021&q=poc+acid+radiocarbon+isotopes&hl=en&as_sdt=0,5 a quick search. Druffel particularly

References old throughout"

RE: Thank you for your suggestions. Recent papers on acidification effect and RPO have been added throughout the MS.

p2, L40, "thought to. The language throughout is a little clunky, better words could be used for readability. Small edits for this though."

RE: Done as suggested. The language of the MS has been improved according to your comments.

p3, L67, "I agree with the other reviewer that the sample names are very confusing, as are the EC labels.".

RE: Now has been addressed throughout the context. According to your and R1's suggestions, sample IDs are not specified. SR1/2 and Sed1/2 are used to present four samples. The methods and the Table 1 in the main text have been refined to mainly focus on major variables in the discussion section. EC labels have been removed and replaced by direct expressions throughout the MS.

p3, L71, "how? by hand or in a proper machine that really does homogenize?".

RE: Two sediments were ground by agate mortar and pestle until no coarse grains were observed. Two sedimentary rocks were ground by zirconic puck mill. Throughout the experiments, samples were homogenized by hand for several times to avoid artificial biases before acidification. Machines were not used due to limited amount of sample material and anticipated loss during processing. To verify our findings, a part of samples (e.g., SR2 acidified by 2N acid rinse) were processed parallelly 2-3 times during a one-month interval. The reproducibility of RPO thermograms is always good, suggestive of insignificant bias from sample heterogeneity.

p3, L87, "Did you analyse the supernatant? Ignore if below - it would be nice to say what happened with the supernatant afterwards. Maybe you could have counted the loss of OC in the supernatant, with your methods there was bound to be OC in it. If you did this below state something here. If not, it's maybe something to think about for a repeat experiment (but not essential really for this paper IMO, Ed's decision).".

RE: Thank you for your valuable suggestions. It is of great significance to analyze the supernatant to indicate the amount and properties of OC leached to the solution. It can be a very good perspective to compare the residual OC in the acidified sediments with soluble OC in the supernatant (to see if the loss of labile OC increases with HCl concentration). A couple of previous studies showed very interesting results about the supernatant as well.

The analysis of supernatants has not been conducted by far for the processed samples. Although it is improper to include all the results (sediments and supernatants, bulk and RPO) in this paper

for the comparison of RPO pretreatment conditions, the supernatant results can be expanded to another comprehensive study with bulk parameters and other analyses as you suggested. Therefore, we agree with you about the merits of analyzing OC in the supernatant but decide not to include the result in this current paper.

p4, L107, "Another word that isn't suitable here.".

RE: The word "impotent" has been revised to "inefficient". The sentence has been rephrased according to another reviewer's suggestion.

p4, Table 2, "Without more obvious codes that shows what the samples are, this is way to hard to really interprate without going back and forth."

RE: The sample codes have been simplified according to your and R1's suggestions. As the MS has been revised to focus on RPO results, Table 2 is moved to the supplementary file. By eliminating confusing sample codes and too much data displayed, the clarity and readability of this paper has been improved. After revisions, the interpretation of the data would be primarily based on RPO thermograms in the figures without too much effort to move back and forth.

Also, you present the RPO stuff here, when most of the above is about Acid methods. I agree with R1 that this should maybe should be two papers, or else change it to balance the acid methods with the RPO methods."

RE: This paper has been reorganized to mainly focus on RPO results. It is necessary to emphasize that bulk and RPO analysis were conducted concurrently for each acidified sample. For instance, ~ 500 mg of a raw sample was acidified, dried, and ground into powder. 20 mg of acidified sample was used for TOC and $\delta^{13}C$ analysis while 100 mg of the same, acidified sample was used for RPO analysis. Therefore, bulk and RPO results present the OC properties of the same sample. In tandem, two different analytical tools can reveal the impacts of acidification on OC properties from different aspects.

Despite the discussion above, we fully agree with your and R1's comments that two parts in the original MS (bulk data and RPO data) were not well joined and transition from TOC and $\delta^{13}C$ to RPO data interpretation lacks a smooth connection. One of the problems is the introduction and method sections were primarily about acidification and bulk parameters. To address it, the introduction section was rephrased to focus more on acidification and the understudied impacts of acidification on RPO data interpretation. We also greatly appreciate your insightful suggestions to incorporate bulk results and more analytical tools into another paper in the future.

p7, L131, "It's not pyrolysis then it's ramped combustion. which is fine, and probably a good choice, but you need to change the term."

RE: Thank you for the reminder. Yes, it is ramped combustion with oxygen supplied in this

study. The term "charring" here highlights that the RPO system in this study is supplied with oxygen to avoid charring as observed in other studies using pyrolysis. Yet, it is not clearly clarified in the MS. To prevent confusion, we have revised the sentence in line 194 and added another relevant reference to improve the clarity, as:

"This sub-oxidation mode was consistently adopted in this study to circumvent possible charring during pyrolysis as illustrated by previous studies (Huang et al., 2023; Stoner et al., 2023; Williams et al., 2014)."

p9, Fig 1, "Have the labels changed? Again, it's hard to read this without going back and forth. I actually have two copies open so I can look at them without going back and forth, it's really not easy to interpret - and with so many methods maybe another reason to spilt the paper."

RE: The labels have been changed as mentioned above. We fully agree with you that the labels and methods here are confusing and hard to follow. As the focus of this paper is about RPO results, this figure has been removed due to limited discussion on it. For the rest of this paper, sample and method codes have been consistently revised to enhance readability. We agree with your idea that splitting the paper may be a good choice.

p10, L201, "I would actually would have liked to see C/N results to show what changes in that would be. It would show more about what is lost. Again, looking at the supernant or what was lost would have been good.".

RE: We fully agree with your suggestions. Detailed elemental composition (e.g., C/N) of acidified sediments can be more informative than TOC and $\delta^{13}C$. The further analysis of residual sediments and the supernatant would be a very interesting part to see in the next stage of the experiment. Hopefully, it can be expanded into another comprehensive study. In this specific manuscript, this part of discussion has been removed. Nonetheless, considering your constructive suggestions, some discussion about the bulk parameters has been incorporated into the implications in the revised MS.

p10, L211, "I would have expected this as the labile OC would have been mostly lost with acid treatment that would not really have been caught by bulk isotope results, which are a mean of many mixtures so not really informative.".

RE: Thank you for the insightful comment. The loss of labile OC is expected during acid treatment, which is supported by the TOC data. However, the changes in bulk isotope values are not significant in this study, since the bulk isotopes are a mean of many mixtures as you suggested. This point has been mentioned in the introduction and conclusion sections to highlight the merits of utilizing RPO analysis to reveal what is lost during acidification. In addition, conducting analysis of supernatant can provide essential information about the amount

and the properties of acid-soluble OC.

p11, Fig. 2, "codes again, I've forgotten which samples are what again. The caption could be more informative.".

RE: The legends have been revised throughout to be more informative (e.g., 1 N rinse instead of EC-1) to directly relate thermograms to experiment conditions.

p11, Fig. 2, "It's also hard to see the difference in colours, especially if printed out in black and white if anyone does that anymore.".

RE: We agree with you the differences in colors are insignificant, making it hard to distinguish. All figures in the revised MS have been refined with more contrast colors to highlight the differences.

P13, "The paper is very long, at this point I had to take a break to get back to is. I do think this should be reduced or split into two papers.".

RE: We agree with you this paper is too long to follow. As suggested above, we have split this paper into two and mainly focus this revised version on RPO results. Accordingly, some introduction and discussion of bulk parameters have been removed to improve the flow of this paper.

p13, Figure 3, "As someone who is lightly colourblind I can't see the differences in these lines at all.".

RE: The colors of the lines in Figure 3 (now Figure 2) have been changed to blue, orange, and purple. The selected colors are expected to be colorblind-friendly with sufficient contrasts.

p14, L291, "I thought you said above that it didn't affect it with the catalysts in the furnaces?".

RE: This point has now been exactly mentioned in Sect. 2.5 but in a different way. For samples after acid rinsing, most of $CaCl_2$ was removed through repeated water rinsing. Conversely, $CaCl_2$ remained in sediments after acid fumigation. According to the experiments in this study and the results of other tests in our laboratory, too much $CaCl_2$ in sediments (basically for acid fumigation) is corrosive for the catalytic wires. There were several lines of evidence to support it. First, the lifespan of catalytic wire in RPO system significantly decreases from several months to less than a few days after processing $CaCl_2$-containing samples. Second, the yield of CO_2 declines significantly after the corrosion of catalytic wires, which was also mentioned in the paper. Third, as shown in the supplementary file, there were some black matters (likely black carbon due to incomplete combustion) adhering to the quartz reactors after processing acid fumigated samples. Overall, $CaCl_2$ does have impact on the catalytic wires, which should be noticed and carefully considered in RPO analysis.

p14, L291, "If it does really effect the method (I'm actually surprised that you got graphite from some of these) this is an impact that people should know about. It's buried here and if papers were separate it would be easier to see.".

RE: Thank you for your insightful comments. As you suggested, this is an important issue that should be noticed. Since there has been detailed discussion on the corrosive effect of $CaCl_2$ in the main text (e.g., in Section 3.2), it would be clear after the paper is split as you suggested.

p14, L294, "FTIR or some other method to show what was actually in the sample would be informative".

RE: Thank you for the valuable suggestion. FTIR analysis would be very useful to reveal the OC composition and organo-mineral interactions in the sediments and is likely informative to link the laboratory observations to specific mechanisms. We would like to incorporate this point in the second paper in the future.

p14, L302, "I think that the paper jumps around too much, this is back to methods again. I think even with two papers, this needs to be cut down and reorganised."

RE: We agree with your concern regarding the coherent narrative of the structure. The detailed description of the $CaCl_2$ addition experiment has been moved to the Methods part as subsection 2.5.

p14, L315, "so basically don't use RPO on samples treated by acid.

Or is there a solution with changing the catylist? Like Ag for S?"

RE: Acid treatment is basically necessary prior to RPO analysis to remove inorganic carbon. Considering the likely influence from inorganic carbon on data interpretation (e.g., Sed2 in this study, Supp Fig. S5), acidification is typically adopted to remove IC. According to the comparative experiments in this study, acid rinse with 1 N HCl is generally a good approach to maintain relatively pristine OC properties. Acid fumigation is not recommended for RPO analysis as too much $CaCl_2$ would bias the result.

Changing the materials of the RPO catalytic wires may be an alternative choice. Yet, it is hard to say whether the performance of the new catalytic wire and the robustness of results can be improved significantly. Additionally, the effect of chlorine on catalysts is evident and the possible solution to this is tricky though. Therefore, the good choice at present is to improve the acidification and other pretreatment protocols for RPO analysis. We suppose the influence of Cl or S on the catalytic wires can be illustrated by SEM or other analyses. In the meantime, we are considering other potential reagents for the removal of Cl and S in our RPO system.

p17, L346, "what about the same for RPO?".

RE: The conclusion part has been revised to focus more on RPO. Besides, we incorporate some insightful points (something like implications) according to your comments. The conclusion part has been further revised according to your and R1's suggestions.

All your suggestions and concerns have been carefully considered and addressed. Thank you for your time and effort invested in reviewing our MS.

References cited

Jez, E., Bravo, C., Lestan, D., Gluhar, S., Martin-Neto, L., De Nobili, M., and Contin, M.: Changes in organic matter composition caused by EDTA washing of two soils contaminated with toxic metals, Environ. Sci. Pollut. Res., 28, 65687–65699, https://doi.org/10.1007/s11356-021-15406-z, 2021.

Dear Mr He and Profs Yang and Cui,

Thanks again for your replies for comments and suggestions raised during the first review of your manuscript and for the revised version. Following the splitting of your manuscript and focusing the present manuscript on the pyrolysis oxidation part, I have sent your manuscript for another review. We have received three reviewer reports this time, including one reviewer who has reviewed this paper before. All reviewers are very positive about your manuscript and I agree with their feedback. Based on their comments and suggestions, only minor revision is required, which will further improve your manuscript. Therefore, I invite you to address the feedback that has been received before I make a final decision.

Thanks for these changes and looking forward to your revised manuscript.

Kind regards
Dr Sebastian Naeher
Associate Editor, Biogeosciences

RE: We sincerely appreciate your assistance in processing our manuscript and are grateful for your consideration of our work for publication in Biogeosciences. We have carefully addressed all the specific suggestions and concerns raised by three reviewers. Please find our point-to-point replies to each reviewer in the response file and the revised manuscript.

Referee #1

This revision of the MS very successfully clarifies that the MS is about carbonate removal methods prior to RPO analysis. The text is much clearer and reads well with some editorial changes needed. Specific suggestions are included below.

RE: We sincerely appreciate your positive feedback and constructive suggestions. Please find our point-to-point replies to your specific suggestions below.

Late in my review I read the response letter and learned that the TOC and carbon isotope data might be published later. That is great. I have an issue with Line 52 of the MS which states "Using RPO analyses supplemented with bulk measurements (TOC and δ13Corg), we assess the potential…" – BUT the only actual mention of carbon isotope data is in Table S2. There is no discussion of the carbon isotopic data in the manuscript. The issue can be solved by REMOVING "supplemented with bulk measurements (TOC and δ13Corg)," from Line 52. If the portion of the above sentence is removed, the data can be left in the MS even though it is not discussed.

RE: We agree with your comments and believe that TOC and δ^{13}Corg results would be interesting as well in a future paper. In the sense of current paper, we decided to focus on RPO result, which is not closely related to TOC and isotopic data. Therefore, we have removed the misleading expression in Line 54 according to your suggestion.

In a future paper I would like to see the statement seen in the original MS Conclusions that rinsing of high carbonate samples with liquid acid was the best pretreatment for carbon isotopic analysis of organic carbon. I actually referred people to the pre-print with this in mind. I would like a paper to easily refer people to in the future.

Jason Curtis, Sept 17, 2025

RE: Thank you for your thoughtful consideration and positive evaluation of our work. Although the detailed discussion about TOC and isotopic results is not included in the current paper, we think with some other additional analyses it will make a great scientific contribution accordingly.

Line 7 - Remove "The" – very first word in the abstract

RE: Corrected in Line 7.

Line 8 – Be clear as to what "characterizing sedimentary organic carbon" means.

Concentration? Labile versus refractory? Isotopically? Etc.

RE: Thank you for reminder. It has been revised to "characterizing sedimentary organic carbon provenance and reactivity".

Line 8 – Same as above. “bulk carbon and molecular-level analyses” Bulk what, molecular what analysis. See similar comment for line 101.

RE: We have revised it to “bulk carbon isotopic measurement and molecular-level biomarker analyses”.

Line 15 – “Notably” not quite the right word. Maybe “Generally, results from…”

RE: Done as suggested in Line 16.

Line 37 Remove - “Moreover”

RE: Done as suggested in Line 38.

Line 68 – “additionally” should be removed

RE: Done as suggested in 69.

Line 69 needs work “and temperatures, the potential influence of heating” Maybe “…and drying temperature to understand potential influence…”

RE: We intended to convey the potential influence of reaction temperature rather than drying temperature. To resolve this, we have revised this sentence to “and temperatures, heating during decarbonation and prolonged exposure to concentrated acid.”

Line 70 “furthermore” is not the right word. Use “Additionally” or similar

RE: Corrected in Line 71.

Line 79 – “to be neutralized” should be “until neutralized”

RE: Corrected in Line 80.

Line 80 – what mass of sample?

RE: For acid fumigation, we basically used the same sample mass as acid rinsing to ensure sufficient sample for measurements. The phrase “(> 200 mg)” has been added to state the sample mass we used.

Line 83 remove “beneath”

RE: Corrected in Line 84.

Line 84 “This is based on the former practice that” - should be “this is because previous studies have shown …”

RE: Corrected in Line 85.

Line 88 and further – Comment – I still contend that freeze drying, air drying, or oven drying fumigated samples does not remove the HCl. It simply removes the water from the sample. It leaves residual HCl. And this residual HCl is strong. This is rarely noted in papers.

RE: We agree with your comment. We have added some discussion about this point in Section 2.2 and Section 3.2 (Line 95 and 242).

Line 94 – "Aside" is awkward. Maybe "alongside" but this is not perfect either.

RE: Now has been revised to "were oven dried with sodium hydroxide flakes being placed alongside".

Line 98 – What does the "§" symbol refer to?

RE: Now has been added in Table. 1.

Line 98 – remove "to be" – not needed

RE: Done as suggested.

Line 101 – What does "bulk" analysis refer to? Bulk %CaCO3?, bulk total lipids, bulk cholesterol? I think that it means bulk d13C but this needs to be clear

RE: Thank you for suggestion. Now has been revised to "bulk carbon isotopic measurement and RPO analysis".

Line 102 – Again, what does "bulk carbon measurement" mean. Should be "bulk carbon isotopic measurement".

RE: Corrected in Line 106.

Line 102 – change "placed" to "placed into"

RE: Corrected in Line 107.

Line 104 – IRMS should probably be a Thermo Electron. Corporation name in China might be different than I am used to. Check this.

RE: Thank you! We have checked the instrument information and corrected it.

Line 105 – Call for table 2 should be Table S2 – CHECK calls for tables throughout.

RE: Corrected in Line 110.

Line 106 – change to "measurement of usgs40"

RE: Corrected in Line 112.

Line 110 – "with thermocouples mounted". "mounted" seems unnecessary.

RE: Corrected in Line 116.

Line 115. If the 5% O2 is 95% Helium and 5% O2 just write this. Don't simply use "diluted" which does not tell anything about what it was diluted with. I later learn from the Sup info and the diagram that it is O2 mixed with He.

RE: The 5% O_2 used in our RPO system is mixed with N_2 rather than He. Information about gas composition has been added in Line 122.

Line 115 continued – I don't see how the gas inputs in the text match up with the gas inputs in Fig S1.

RE: Thank you for pointing this out. As shown in Figure S1, there are two gas inlets. The first one ($He+O_2$; at the top) is introduced directly into the upper quartz reactor, while another flow ($He+O_2$) is supplied to the lower part of the reactor through the outer quartz tube. During conventional analysis, we normally use a gas composition of 27 mL min^{-1} He + 3 mL min^{-1} 5% O_2 for the upper reactor and another 5 mL min^{-1} O_2 directly to the lower furnace. However, for any unconventional analysis, the gas composition can vary depending on situations, given the installation of both O_2 and He supplies in upper and lower furnaces.

Line 116 – define "sub-oxidation mode" – probably what was described before but not clear enough

RE: The phrase "sub-oxidation mode" means that the O_2 concentration (0.5%) used in this study is lower than the concentration of oxidation mode but still higher than pyrolysis (O_2% = 0). Information about O_2 concentration has been added in Line 122.

Line 116 – "adopted" maybe should be "used"

RE: Corrected in Line 122.

Line 122 – "Notably, the residual chloride in sediments" should be "Residual chloride in acidified sediment samples"

RE: Corrected in Line 131.

Line 124 – "This consideration was of no concern to" should be "Residual chloride was of no concern for because it was already removed"

RE: Corrected as suggested in Line 131.

Line 124 "rinsing" should be "rinsed"

RE: Corrected in Line 131.

Line 125 – "counterparts" should be "samples"

RE: Corrected in Line 133.

Line 125 – "surged the risk" – should be "increased the possibility of damage to catalytic wires"

RE: Corrected in Line 133.

Line 126 “as the standard” probably not needed

RE: Now has been revised to “we ran an in-house standard sample” in Line 134.

Line 130 – “the in-house standard (Irati T2)” should be “Irati T2”. End the sentence here

RE: Corrected.

Line 130 – Start a New sentence. Change “…by assuming that chlorine gas is generated…” to “We assume that chlorine gas generated…” (no need for “is”)

RE: Corrected.

Line 138 – “Based on aforementioned” should be “Using the aforementioned”

RE: Corrected in Line 147.

Line 158 – “gradient of HCl concentrations” should be “gradient of HCl concentrations used for sample acidification”

RE: Corrected in Line 170.

Whole sentence from Line 156 to line 158 – “Although variations” Remove “Although” - Then later – “and S4), thermographic patterns” should be “and S4) PERIOD then start a new sentence. “Whereas thermographic patterns”. (split sentence into two. This will help to emphasis the second sentence.)

RE: Now corresponding changes have been made.

Line 159 – “To illustrate the inherent consistency between thermograms and HCl concentrations being applied” remove “inherent” and change “being applied” to “HCl Conc used to acidify samples”

RE: Corrected in Line 171.

Line 169 “In contrary” should be “In contrast”

RE: Corrected in Line 181.

Line 170 “has been” should be “was”

RE: Corrected in Line 182.

Line 183 – Use “as aggregates”

RE: Corrected in Line 194.

Line 190 – Include which metal are isotopically fractionated.

RE: Now has been included in Line 203.

Line 215 – “forms” should be “formed”

RE: Corrected in Line 228.

Fig 2 – "(a), (b), (c) and (d) represent subsamples" Maybe change to "Panels (a), (b), (c) and (d) are subsamples…"

RE: Corrected.

Line 224 – "Powders" adds confusion. I suggest using "Samples"

RE: Corrected in Line 237.

Line 241 – "other" should be "rather"

RE: Corrected in Line 255.

Line 259 – "held by" should be "found in"

RE: Corrected in Line 273.

Line 264 "Former studies" should be "Previous studies"

RE: Corrected in Line 278.

Line 268 "overlain together" is repetitive. "Overlain" is sufficient.

RE: Corrected in Line 282.

Supplementary

Fig S1: "The" schematic – remove "The"

RE: Corrected.

Fig S1 "and the corresponding thermogram" should be "and a representative thermogram"

RE: Corrected.

Fig S2: Suggested changes "Normalized thermograms of the standard sample (Irati T2) analyzed before and after analyses of acid-fumigated subsamples. No obvious shifts are observed when comparing the thermograms."

RE: Corrected.

Fig S4 – Initially I had no idea what FD means. Determined that it is Freeze dried. No clue what heat is if it is not oven dried. Define FD, OD, and heat in the caption.

RE: Now all definitions have been added.

Fig S5: The "shot" should be the "Image" or the "photograph"

RE: Corrected.

Fig S5 Continued – "The black remnants are likely sourced from the incomplete" should be

“The black remnants are likely a result of incomplete”

RE: Corrected.

Fig S6 – I suggest using “Raw sample” or “original unmodified sample” instead of “raw aliquot”

RE: Corrected.

Table S2 – I would suggest adding to the caption something like “See Table S1 for definitions of different experiment conditions (EC numbers)”

RE: Now has been added in the caption. All specific comments have been addressed. We appreciate your valuable suggestions.

Referee #3

Review of He et al. “Technical note: Assessing pretreatment approaches for serial pyrolysis-oxidation analysis of sedimentary organic carbon” (egusphere-2025-701)

Overall, I find this manuscript to be well written and the results clearly presented. I am satisfied with most aspects of the study and believe it is suitable for publication.

RE: We sincerely appreciate your positive feedback. Please find our point-to-point replies to your specific comments below.

I would only suggest the author to consider addressing two minor points:

Table 1: I was a bit confused. In the Method sections, the authors mentioned several different dying methods, temperatures, but only some are shown here. Probably explain why were these particular conditions chosen as the main experimental setup? From my experience, the oven drying is still a common method for treating these acidified samples?

RE: Thank you for the comments. We would like to state that we have considered different conditions (including oven drying and different temperatures) as you mentioned. In the first round of review, all different experimental setups were included in the main text. However, we felt it a bit lengthy to put all conditions and discussion together in the main text. Thus, main experimental conditions (acidification method and aqueous HCl concentration) were determined after we thoroughly compare all results. According to your and another reviewer’s comments, we have added a brief discussion on other conditions that were not included in the main text starting from Line 167.

Section 3.3: Besides concluding that acid rising is more effective to maintaining sediment pristine conditions, there appear to be substantial differences between low concentration acid rising the pristine samples. I suggest adding more discussion on this point.

RE: We fully agree with your idea that samples rinsed with low concentration HCl were not completely identical with the pristine samples. This can be attributed to: 1) overestimating thermogram of raw sample due to decomposition of carbonates at low temperature (<450°C), 2) OC loss during acid fumigation. We have further added some discussion on this point in Section 3.3.

With these small clarifications, I fully support acceptance of the manuscript.

RE: We have addressed all your specific comments. Thank you for your valuable suggestions.

Referee #4

Assessing pre-treatment approaches for serial pyrolysis-oxidation analysis of sedimentary organic carbon

Summary

He et al. present an evaluation of different sample pre-treatment methods for ramped-temperature oxidation/pyrolysis analysis. Considering that ramped-temperature oxidation/pyrolysis is becoming more widely used, the information presented in this manuscript are useful and timely. I found the results of the experiment with CaCl2 addition particularly interesting. The manuscript is well written and organised, and properly referenced. There are some aspects that can be improved significantly:

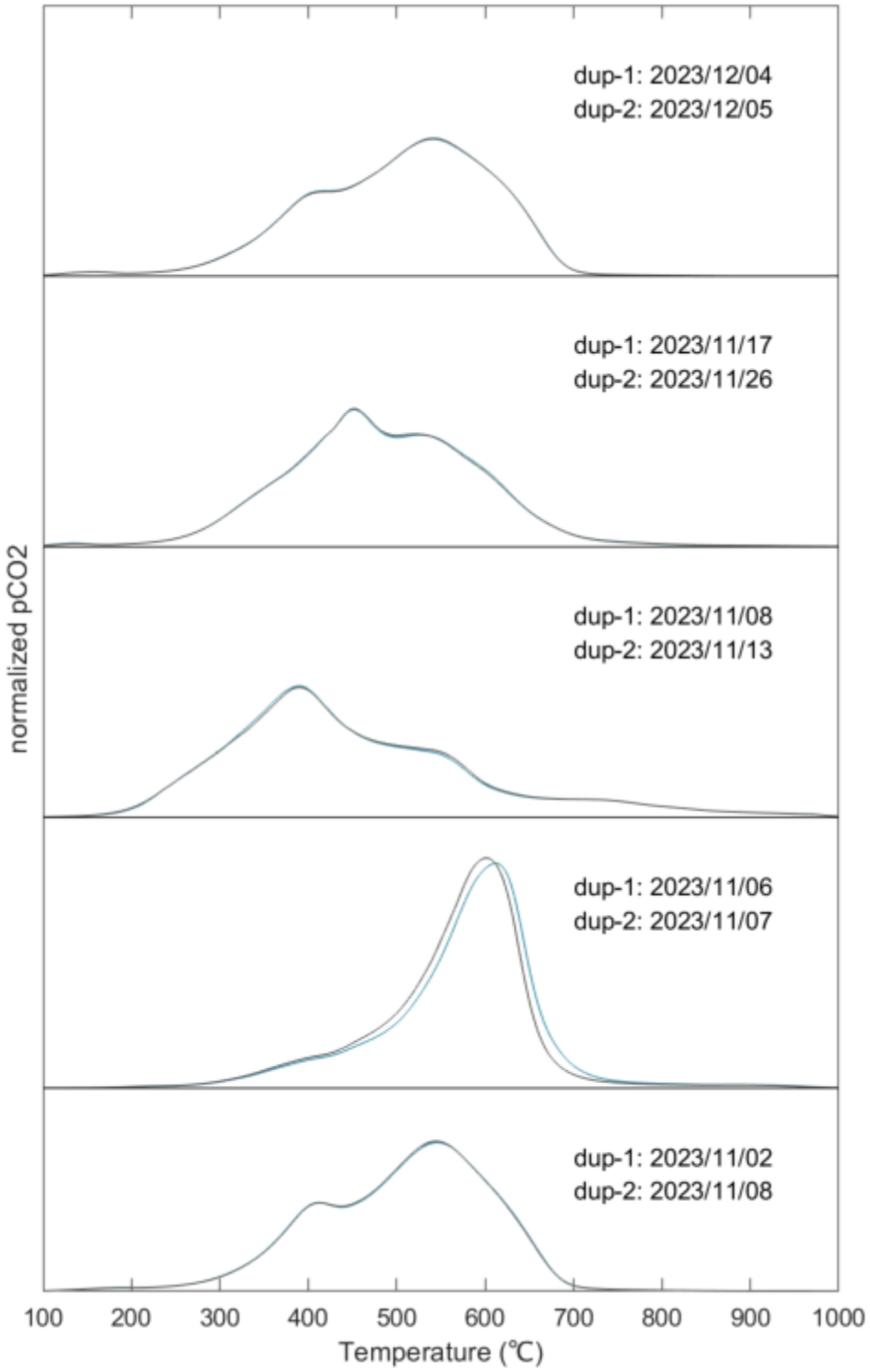
RE: We sincerely appreciate your positive feedback. Please find our point-to-point replies to your specific comments below.

1. The title can be misleading. All samples were analysed using oxidation mode only. Do the authors expect to observe similar results when using pyrolysis mode? Perhaps they can include a clarification/suggestion in the conclusions.

RE: Thank you for your insightful comment. We have added a clarification in the main text (Line 306) and would like to add some explanations here about the title of this study. Although we only used oxidation mode in this study, the same observations and main conclusions are expected to be identical or similar when using pyrolysis mode. Secondly, O_2 concentration in direct contact with the sample is much lower than previous studies that applied oxidation mode. Therefore, given the trace oxygen level maintained throughout the analysis, reactions in the quartz reactor are more similar to pyrolysis process (though it is indeed not pyrolysis). When vaporized OC is carried out of the reactor by the carrier gas, it will be instantly oxidized by pure O_2 and be converted to CO_2. In conclusion, this is the pyrolysis-oxidation process mentioned in the title. We have also added the annotation "pyrolysis" in Supp Fig. S1 for readers to understand the reactions happened in the reactor.

2. Lack of replication. It would recommend a strong justification of why replicate analysis were not carried out. Can the authors include data in the supplemental material that justifies not running replicates?

RE: In fact, we ran replicates throughout the analyses of each batch of samples, of which the point was not included in the main text. Here we provide a figure to exhibit the replicate results.



As shown in the figure, thermograms of most replicates are entirely overlapped, suggesting great reproducibility throughout the analysis. However, this is not included in the main text as the reproducibility of replicates are indicated with the in-house standard sample (Irati T2) in the supplementary file. In fact, the Irati T2 standard sample was measured periodically to secure the reliability and reproducibility of data.

3. There should be a separate results and discussion section for the results of reaction time,

drying methods and drying temperatures. These results are important and should be discussed accordingly. If the authors consider that they do not have enough data to do so, perhaps they can be removed them from the manuscript.

RE: We agree with your idea that other conditions are important in processing samples. A very brief discussion has been added in Section 3.1 to show the results (Line 167). Unfortunately, the detailed discussion concerning these factors has been removed after the first round of revision to streamline the overall content. We would like to incorporate them into another future paper.

4. Activation energies are not discussed. I think the authors are missing the opportunity of discussing the impact of the pre-treatment methods on the activation energies of the samples (both mean and standard deviation), and from each activation energy intervals (or temperature fractions). It is possible that although there are both carbon loss and chemical alteration during treatments, they result in similar activation energies (within uncertainties). Then the questions are whether to work with the thermograms or activation energy distributions, and the impact on radiocarbon results for each fraction.

RE: Thank you for your insightful consideration. We completely agree with you that activation energies (E) are very important parameters in a paper that primarily focuses on RPO analysis. There are three main reasons for not including too much discussion in the paper. (1) Thermogram is a more straightforward way to reveal changes compared to activation energy. For example, two completely different thermograms can result in identical mean E value. However, any small change can be clearly exhibited by thermograms. Additionally, it would make the paper lengthy by including too much discussion on activation energies. (2) Parameters of activation energies are comparatively more sensitive to noise. A drift of 10-20 ppm in the baseline at high temperature can mask any nuanced shifts in low temperature. In contrast, thermograms are more resistant to any noise in the system. (3) Thermograms are more easily to be scaled, facilitating the direct comparison between raw samples and acidified samples as shown in Section 3.3. In comparison, distributions of activation energies are affected by different reaction kinetics of carbonates (also see reply below), inhibiting direct comparison when including raw samples. Overall, it is more reasonable to focus simply on thermograms when carrying out discussions. Meanwhile, we argue that the optimized pretreatment conditions as suggested in this study would benefit the broader application of activation energies in future studies.

Radiocarbon results for RPO fractions are as important as RPO thermograms. It is a pity that we did not carry out radiocarbon analysis of different RPO fractions in this study. It is especially interesting to compare the fractional radiocarbon data for acid-rinsed and acid-fumigated samples, given the significant differences between thermograms in our study. Some previous

studies have preliminarily studied on the methodological impacts on radiocarbon analysis (Bao et al., 2019; Plante et al., 2013). Therefore, future studies can merit on previous and current study to systematically probe the mechanism.

5. Line 236. What are the mechanisms in which chlorine can influence thermochemical reactions of organic matter?

RE: Chloride is shown to react directly with catalytic wires, which further impacts the efficiency of oxidizing C to CO_2. Furthermore, it is likely that chloride is converted to reactive chlorine during heating that accelerates OC decomposition. However, the reaction complexity is beyond the scope of this study.

6. Line 271. Does the activation energy value of 182.48 kJ/mol correspond to a non-acidified sample that contains carbonates? If that is the case, please check Hemingway et al. (2017) about the limitations of calculating activation energies with the rampedpyrox package. I believe first-order kinetics model should not be used when carbonate is present.

RE: We appreciate your expertise and insightful suggestions. It is misleading to use the mean activation energy of unacidified sample as carbonate decomposition does not follow the same reaction kinetics as OC decomposition. To resolve this, we revised the expression to "*relatively lower T_{max} value of raw Sed2 sample compared to the corresponding acidified samples*".

7. Line 288. Please specify the concentration of HCl or range of concentrations. Using the term "diluted" here is inappropriate.

RE: Now has been revised to "1 N" in Line 306.

8. Are the results of Fig S2b post-fumigation and rinsed? Please specify

RE: We conducted a systematic comparison of Irati T2 before and after analysis of each acid-fumigated, oven-dried sample. Specifically, samples are analyzed in such order: Irati T2 (pre-fumigated samples) → SR1 (acid fumigation) → Irati T2 (post-fumigated samples). It is designated to capture any noticeable changes after running acid fumigated samples. Accordingly, Fig. S2 is not the results of post-fumigation and rinsed, but the comparative results of Irati T2 before and after running acid fumigated samples.

We have addressed all your suggestions and concerns. Thank you for your valuable suggestions.

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