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 decide to split this MS to 2 papers. The revised MS will mainly focus 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 careful 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 material to complement our overall conclusions.
(3) Moved the second Table (Table 2) to the supplementary material 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.

"strikingly discrepant" – "Strikingly different"

RE: For clarity, "strikingly discrepant differences" has been corrected to "striking differences".

"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 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.

"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".

"exhibit constant gradation" ?

RE: Now has been corrected to "exhibit consistent shift". Similarly, "systematic gradation" at p10, L219 has been corrected to "systematic changes".

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

RE: Now has been revised to "Overall, …".

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 material 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" 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 starting from p4, L107, as:

"Fumigated subsamples were dried at 60 ℃ given that lower temperature is inefficient to remove water vapor since the fumigated subsamples is prone to absorbing water."

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 material 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 material.

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. We would use the current line numbers to ensure the quickly locate the revisions in the pre-print and use new line numbers (that after revisions) in our final response file. Please find our revisions/replies below.

<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., $\delta^{13}C$)."*

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."*.

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."*.

p1, L19.

RE: Changed to "*... are more similar to the raw materials*".

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.

p2, L37-38.

RE: The expression has been corrected as suggested.

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. 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: Done as suggested.

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.

p3, L90.

RE: Done.

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.

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.

Section 2.3

p5, L116.

RE: Corrected.

p5, Table 2.

RE: The Table 2 has been moved to the supplementary material (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.

p7, L134.

RE: Done.

p7, L136.

RE: Done.

Section 2.5

p7, L144.

RE: Corrected as suggested.

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 more times in discussion and conclusions sections to remind the readers. Thank you for your suggestion.

p10, L214.

RE: Done.

p10, L216.

RE: Done.

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.

p12, L264.

RE: Done.

Section 3.3

p13, L285.

RE: Corrected.

p14, L293.

RE: Done.

Section 3.4

p16, L334.

RE: Done.

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.

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.

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.*"

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

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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.