Response to Reviewer #1

(comments by the reviewer are printed in italics, our point-by-point response in blue)

Reviewer #1 (Remarks to the Author):

Overall well structured. detailed revisions in the supplement.

We thank Reviewer #1 for her/his positive assessment of our manuscript.

really glad you used sample of this place. but it is a bit less known then Congo Basin. can you add some more information? or simply write Alpine lake Cadagno? otherwise the reader is lost. you go in details later but as a first reader I can better understand if you add "alpine." just give an idea

Thank you for the suggestion. We have corrected it as “Alpine Lake Cadagno” in the revised version.

overall the introduction is well structured and clearly motivates the study by outlining the limitations of existing approaches and defining a clear methodological gap that the proposed analytical framework is well positioned to address. check minor spelling / spacing

We thank Reviewer #1 for her/his positive assessment of our manuscript. We have corrected all the spelling and spacing errors in the revised version.

general iron or specially the one bio-available? you mean all. species right? the one lock in the minerals and reduced and also the one partially absorbed in bio mass. maybe clarify a bit. one sentence is enough.

Thank you for your thoughtful and precise comment. You are correct that our original phrasing was ambiguous. We referred to all redox-active iron species—including iron locked in mineral lattices (e.g., Fe(II) in silicates, oxides, and sulfides such as pyrite), as well as iron complexed within or adsorbed onto organic biomass. In the context of our high-temperature oxidation method, the protocol measures the total oxygen demand arising from the complete oxidation of any reduced iron, regardless of its bioavailability or specific mineralogical host. We have revised the main text accordingly.

that is so cool!

We thank Reviewer #1 for her/his positive assessment.

Carbon Oxygen Sulfur molecules right?

COS is carbonyl sulfide.

no map because it is a technical note article correct?

You are correct.

good, but meromictic is quite a technical wording and later you explain what the lake is. not sure if it is needed. who is your audience? limologist? then leave it if you are planning for a broader audince remove.

Thank you for your suggestion. You are right that “meromictic” is a technical term. Our intended audience includes not only limnologists but also broader Earth scientists, biogeochemists, and paleoenvironmental researchers. To improve accessibility without losing clarity, we have removed “meromictic” in the revised version.

minor point: instrument names are given using branded products names. For consistency and formal style, the authors may wish to standardize instrument descriptions using model and manufacturer names without trademarks-style wording. add the trade mark

Thank you for this minor but important stylistic comment. We have revised the instrument names with branded products names and ensure that instruments are clearly identified with manufacturer name and model number, with the trademark symbol placed after the product name as appropriate.

good but confusing. some part of the figures are a bit small to read. I understand the idea but the quality and the size of the writing needs to be increased.

Thank you for this careful observation. We have increased the resolution of the figures and enlarged the font sizes of axis labels, legends, and annotations throughout each panel to ensure full legibility.

similar to the previous comment. trade-mark formatting

Corrected.

check the layout proposed by copernicus.

We have now checked the manuscript layout against the Copernicus formatting guidelines and ensured consistent writing throughout.

this could be part of the previous sections.

Thank you for your suggestion. We agree that this part can be merged into previous sections and we have revised it accordingly.

enabling characterization of their reactive components? precise characterization of their molecular speciation. if I got it right you are not directly measuring molecular speciation - you are ingerring it from kinetics and gas evolution. right?

You're correct. We have replaced "molecular speciation" with "kinetically resolved characterization of C and S phases" throughout the text to avoid any implication of direct molecular-structure identification.

whereas ?

Corrected.

almost interpretation/ discussion. but I think it is good because you give a first input to what might be. I think you can leave it like this

Thank you for your comment.

these are not normed to 1 right? difficult to make a comparison. but maybe you want to show the difference in the thermograms. maybe clarify? or norm them to area 1 as done by Hemingway et al. 2017

You're right that these curves are not normalized to 1. We thank the reviewer for this suggestion. Our intention in presenting the curves in their original form was to preserve differences in the thermogram and evolved gas profiles, including variations in peak intensity and relative amplitudes, which contain information about the abundance and reactivity of different components. Because the signals reflect element-specific stoichiometry as well as differences in detector sensitivity and response among gas species, normalization to an area of 1 could obscure these quantitative relationships. For this reason, we chose not to normalize the curves, as our objective

here was to emphasize differences in both pattern and magnitude rather than compare only the shapes of the distributions.

this is really cool.

We thank Reviewer #1 for her/his positive comment.

here you start with oxidation and then you talks about non oxidative conditions. under non-oxidative conditions, sulfurs volatilizes - it does not oxidize, right? so the part "volatilization and oxidation" under both condition is slightly misleading. if I get it right you want to say volatilization under inert, and volatilization + oxidation under oxidative. right?

Thank you for this precise comment. You are correct that the original text was confusing. Under non-oxidative conditions, sulfur only volatilizes without any oxidation. Under oxidative conditions, this volatilization is accompanied by partial oxidation to SO_2; however, a fraction of sulfur escapes as vapor before complete oxidation can occur, leading to measured d^{O_2} values lower than theoretical predictions. We have revised it accordingly.

minor note: sulfide oxidation behavior can depend on mineral phase (e.g. FeS2 polymorphs vs monosulfides), which may influence the temperature window and shape of mass-loss and SO2 release. If relevant to the natural samples, a brief note on potential phase -dependent behavior (or mineral identity was constrained) could help interpretation.

We fully agree with the reviewer that phase-dependent behavior can influence interpretation of natural samples, but here we refer to a standard pyrite sample (pure, well-crystallized FeS_2).

strong statement! but defensible.

Thank you.

a bit overstated... to me the method distinguishes components kinetically. identifies gas products, but does not identify molecular structures directly. right? I would maybe use "component-specific", "phase-specific" or even better "reactivity-resolved". not molecular in the structural chemistry sense.

We fully agree and have replaced all instances of “molecular speciation” with “reactivity-resolved speciation”.

"completely oxidized" but before you are talking about incomplete sulfur oxidation without secondary oven. you explain later the the oven. either you somehow mention it here to support your statement or you consider carefully the "completely".

Thank you for this precise comment. We now remove the completely in the revised version.

report here which one

Done.

this is repeated 3 times... decomposed into its constituents?

Thank you for pointing out this redundancy. We have rephrased for conciseness.

yielding a well defined

Corrected.

a bit promotional but you can support this statements with the plots Fig. 3

We have referred directly to the Fig. 3.

Minor Point: Because the calibration panels use different mass ranges for H, C, and C, a short note in the caption clarifying that axis limits reflect elements - specific stoichimetry and detector sensitivity could help first -time reader.

Thank you for your suggestion. We have added it to the caption of Fig. 3 accordingly.

a bit misleading. they are no a "direct measure" of a kinetics in a strict sense. safer wording "used to derive kinetic parameters" or "used to characterize reaction kinetics"

We fully agree and have revised it as “our approach use pyrograms to characterize reaction kinetics…”

All non-isothermal solid-state kinetics are parameterized using Arrhenius type expression, but: complex heterogeneous materials rarely follow a single Arrhenius law. that is why you use the apparent Ea and DAEM. here you should make clear that this is an effective parameterization. PS not mandatory, but clear

"based on Arrhenius-type behavior (Eq. 1)"

Thank you for your comment. We have corrected accordingly.

energies ?

Corrected.

"following Hemingway et al., (2017)." ? or "Results were compared with those obtained using a distributed activation energy model (DAEM; Heminway et al., 2017)"

Corrected.

Figure 4 is sound, Information -rich but visually heavy. The wording "apparent" why did you chose it? not wrong but maybe more confusing than helpful. generally consider reducing the number of panels shown simultaneously (A-E, D-H) rest in supplements.

We thank the reviewer for this constructive comment. Following the reviewer's suggestion, we have removed panels B, F and retained the rest in the Figure 4, which are sufficient to illustrate the kinetic validation of our approach.

We chose the term "apparent activation energy" (aE_a) deliberately to distinguish it from a true, fundamental activation energy that applies to a single elementary reaction step. In solid-state kinetics of complex, heterogeneous natural materials (such as sediments containing mixed organic matter, multiple sulfur phases, and minerals), the thermal decomposition proceeds via overlapping, multi-step reactions. The activation energy derived from model-free isoconversional methods or DAEM under such conditions is an effective or lumped parameter that reflects the weighted average of multiple simultaneous processes, rather than a single bond-breaking event.

These results confirm ?

Corrected.

plausible, but: didn't measure directly the molecular structure here, right? it is inferred from the thermal stability. maybe phrase it this way "consistent with more aromatic, thermally stable organic matter" something along these lines

You're right. We have rephased the sentence accordingly.

"proxies that point to a transition" not pointing

Corrected.

Spacing

Corrected.

okay but a slightly promotional. remove or put into the conclusion.

We agree with the reviewer and have removed it accordingly.

here you are interpreting consider to bring it to the discussion section if you want to keep the results separated from the discussion or say "consistent with sulfurization associated with DSR"

We have corrected it accordingly.

increase the size of the font. if possible can you difference between a bit more between samples? the other one as colours which helps a lot

We thank the reviewer's suggestion and have revised the figure accordingly.

small side note try to be consistent with the scale. or state why you chose a different one. easier to understand the two figures increase a bit the size of the writing if possible. colours really good I like this comparison.

Thank you for your comment. We have increased the size and ensured the scales are now consistent.

"specific" or "absolute" redox capacy? be consistent. clarity issue check if you are consistent with this wording

We now use “absolute redox capacity” consistently.

and provides, right? and is missing

Corrected.

are consistent with or closely match - accurately reproduce is strong

Corrected.

reproduce - grammar not reproduces if the you are referring to "our results"

Corrected.

Panel B in Figure & serves primarily as a reproducibility check for the dO2 measurements (really good results!). this could be clarified more explicitly in the caption, or consider move it to the supplement to streamline the figure.

Thank you for your suggestion. We now move the panel B to the supplement.

this is more an interpretation. again in case you plan to separate the Results from the discussion consider to relocate. PS: this is completely plausible and consistent with earlier results.

We agree that the causal attribution (premature volatilization) is an interpretation, not a direct result. Accordingly, we have removed this sentence from the Results section and relocated it to the Discussion section, where it now appears alongside supporting evidence from the secondary oven optimization.

this is really cool! I think it also works, you oxidize everything under controlled lab conditions, reflects total reducible inventory and does not depend on current in situ redox state. right?

Exactly.

maybe phrase "independent of current environmental redox conditions" so this avoids "philosophical" ambiguity.

Corrected.

reaching 95-99% is excellent - but not strictly "complete". the data supports near-compete oxidation. not absolute completeness. so your wording should reflect that. this is not a conceptual flaw rather a tone correction. so you can justify better the results as well.

We thank the reviewer's precise comment and now we use near-compete oxidation throughout.

highlight the importance ?

Corrected.

enables near-quatitative oxidation or even better substantially improves oxidation completeness

Corrected.

Figures 7 conveys several important points regarding oxidation completeness and secondary oven optimization, but combines pure standards and natural samples with different conceptual purposes and dO_2 scales in a single figure. while scientifically sound, the figure is visually dense and somewhat difficult to parse. Consider grouping standards and natural samples separately, or splitting the figure, to improve charity and guide interpretation. so you can have less different scales and also make the figure more readable

We thank the reviewer for this helpful suggestion. We revised Figure 7 by separating the panels into two groups: the first row now presents standard samples, and the second row presents natural samples, with additional text annotations to guide interpretation. This reorganization improves visual clarity and better emphasizes the central point that the secondary oven promotes near-complete oxidation, particularly for volatile-rich materials.

... of total ...; remove "," ; "carbon"; remove ","; consistent with; originating

Corrected.

yes but, not every possible redox component in all sediments. minor suggestion: consider slightly moderating terms such as "providing a detailed", "providing a kinetically resolved" (last one would fit the overall thematic)

We agree with the reviewer and now revised it as "providing a kinetically resolved redox characterization of the thermal reactivity of sediments and minerals."

Figure 8 effectively links oxygen consumption profiles with evolved gas signatures across contrasting samples. However, the central Panels (B/E) are visually dense due to multiple overlaid components and dual axes. Minor simplification or clearer visual separation of components could improve readability without altering the scientific message.

We thank the reviewer for the suggestion. After careful consideration, we have chosen to retain the original layout of Figure 8 because the simultaneous display of multiple components in panels B and E directly conveys the method's ability to resolve kinetically distinct redox phases in a single run. To improve readability, we have clarified the axis labels and substantially expanded the figure caption to guide the reader through each panel and explain the relationship between O_2 consumption and gas evolution. We believe this balance preserves the scientific message while addressing the reviewer's concern about clarity.

why not also Congo? because before was really interesting to see the difference between Congo and Cadagno. Still great work! Looking forward to the next paper.

Thank you for this encouraging comment. The primary focus of this manuscript is technical and methodological. For this purpose, we selected representative samples from two contrasting environments to illustrate the method's ability to resolve carbon speciation (Congo) and sulfur diagenesis (Cadagno), but we deliberately did not attempt a full-profile comparison. A detailed depth-profile from the Congo Basin, is currently under revision for a separate paper.

did you acidify the samples and removed the TIC? not sure to have seen this. or do you define TOC by temperature? like the SoliTOC?

natali et al. 2020, https://www.sciencedirect.com/science/article/abs/pii/S0040603119306136

No acidification was performed. Inorganic carbon is resolved kinetically by its high-temperature CO_2 release (>600 °C); organic carbon is the lower-temperature fraction. We have added a sentence in Section 2.2 clarifying this.

no you do not "identify" the data shows that a depth maximum in SO2 release during oxidation experiments. you infer that this reflects in situ S remobilization and re-oxidation. it is plausible but not directly proven by TGA. I recommend just changing the wording to "suggests", "consistent with". So the reader understands that you infer to this conclusion without overstating.

We thank the reviewer's precise comment and now we use "suggests" in the revised version.

Do you have indipendent meineralogical confirmation (XRD, SEM, etc?) to show what you interpretation is correct? let's see if I get it right. upper zone: multiple peaks means metastable metastable sulfides (ZnS, PbS etc). middle zone: fewer peaks means loss of labile sulfides. Lower zone: you would see the most stable FeS form, pyrite. my issue is that how it is phrased right now wants to say that the activation energy alone is uniquely identifying the ZnS vs PbS. which would be great but you need a way to show it with additional tests. The aEa is indicative but not sufficient alone to say that. I suggest to rephrase "constent with metastable metal sulfides (e.g., Fe monosulfides and trace metal sulfides)".

Thank you for this comment. The reviewer is correct that we need independent mineralogical confirmation, which would be done in the future work. Now we have rephrased exactly as suggested.

"phase"

Corrected.

maybe add some ref. because what you say it true but to support this statement add ref that claim your statement.

Yes, we have added some references to support our statement.

that is a bold statement but fair.

Thank you.

Figure 9 is clear and effective, particularly the aEa distribution in panels F-H. the left -hand panels (A-E), however, combine several variables with different units and interpretive weight into a single stacked view, which is visually dense. maybe consider split the figure or change combine colours with the axis.

Thank you for the suggestion. We have revised the Figure 9 A-E with different colors for clearness.

Maybe "reflect oxidation reactions and associated bond transformations."

Corrected.

"attributed to"

Corrected.

this is a bit a stretch ... as I mentioned before do you have something to back up your statement? this method for what I could read resolves the kinetic components and infers likely phase. but does not directly resolve molecular identity, uniquely identify every single phase, nor provides complete speciation like XRD + MS. this phrase can be misleading. what I would suggest "this approach provides a kinetically resolved characterization of redox-active phases, linking thermal stability and oxygen demand within a unified analytical framework"

The reviewer is correct. We have revised the sentence as the reviewer suggested.

Figure 10 is highly information -dense. something I am missing are the axis from A to D. to the all refer to E? I need to infer units from context. this should be clarified. My advise reduce to E and F rest in supplementary. you can always refer to the supplementary material

We thank the reviewer's comment and suggestion. We revised Figure 10 with y-axis. It serves as a kinetic fingerprint of a representative sediment, highlighting the core innovation of our approach: synchronously resolving thermal stability, evolved gas species and their activation energy distributions in a single analytical run.

"high-resolution"

Corrected.

"not resolvable using bulk analyses alone"

Corrected.

"constraints on paleo-oxygen fluxes" better this

Corrected.

lofty goal! this reads more like a grant proposal ending. may I suggest "Future applications to diverse sedimentary and geologic systems may further refine our understanding of redox processes across environmental settings."

Corrected.

well deserved! good job!

We thank Reviewer #1 for her/his positive assessment of our manuscript.

really minor: check the formating there are some inconsistency with some references some have https:// and or none of. chose if CAPITAL or not.

Corrected.