Response to Reviewer #2

Reviewer #2 (Remarks to the Author):

The article presents an interesting and technically relevant approach to kinetically resolved analysis, and its main conceptual framework is clearly articulated. The authors outline the experimental setup and provide a logical progression from theoretical background to practical implementation. The overall structure of the paper supports readability, and the figures and equations help contextualize the proposed method.

We thank Reviewer #2 for her positive assessment of our manuscript. We appreciate the reviewer's constructive suggestions, which have helped us improve the transparency, reproducibility, and clarity of the manuscript.

Regarding the methodology, it is described in a generally coherent manner; the experimental conditions, measurement procedures, and analytical framework are outlined. However, while the core experimental steps are presented, certain aspects could benefit from greater detail to ensure full reproducibility. For example, although the authors explain the type of kinetic model applied and reference the governing equations, the description of parameter estimation is somewhat concise. It is not always entirely clear how raw experimental data were processed prior to fitting, whether nonlinear regression was performed using a specific algorithm, or what statistical criteria were used to assess goodness of fit.

Concerning the calculation of kinetic parameters, the paper indicates that these were derived from fitting the experimental data to the proposed kinetic model, but the computational procedure is not exhaustively described. The reader can infer that parameters such as rate constants were obtained through model-based regression; however, the manuscript does not fully specify the fitting protocol (e.g., software used, optimization method, weighting strategy, treatment of uncertainty). As a result, while the conceptual basis for parameter calculation is understandable, the practical implementation lacks some transparency.

We thank the reviewer for these important comments. We agree that additional methodological details strengthen reproducibility. In the revised manuscript, we have substantially expanded the Methods section (Sections 2.4) to clarify the complete workflow from raw data processing to parameter estimation.

- **Raw data processing:**

  Raw thermogravimetric and calorimetric data were initially processed using Mettler Toledo STARe software. Prior to kinetic fitting, baseline drift and buoyancy effects were corrected by subtracting blank runs performed under identical analytical conditions, using empty crucibles heated along corresponding temperature ramps. MicroGC chromatograms were analyzed with the Solia software, which quantified evolved gas concentrations by external calibration against known standards (Fig. 3).

- Bulk mass-loss measurement alone does not capture the intrinsic reactivity of complex materials. To overcome this limitation, our approach uses pyrograms, heat-flow data ang gas-evolution profiles to characterize the reaction kinetics of C and S devolatilization and/or combustion pathways based on Arrhenius-type behavior (Equation 1).

  $$k = \mathrm{A}\exp\left(-\frac{Ea}{RT}\right), \tag{1}$$

  where k is the temperature-dependent rate constant, A is the empirically derived Arrhenius pre-exponential ("frequency") factor, Ea is the activation energy, R is the ideal gas constant, and T is the measured temperature (see Table 1 for symbol descriptions).

To extract kinetic parameters, we employed a dual-model approach:

- **Model-Free Isoconversional Method:** First, apparent activation energies (aE_a) were determined using the model-free isoconversional method of Vyazovkin (Vyazovkin and Wight, 1999), implemented within the kinetics evaluation module of the STARe software. This reaction was evaluated the across discrete fractional conversion intervals (α). This approach does not require prior assumptions about the reaction model and served as our baseline for parameter validation.
- **Distributed Activation Energy Model (DAEM):** Second, we compared the isoconversional results with those obtained using a parallel-reaction Distributed Activation Energy Model (DAEM), following the methodology outlined by Hemingway et al. (2017). A critical step in our parameterization was the treatment of the pre-exponential factor (A). Use of a fixed A value led to systematic overestimation of activation energies for certain standards such as calcite that do not follow a first-order decomposition kinetics (Fig. 4). Consequently, A was iteratively optimized across a boundary range of 10^5 to 10^{12} s^{-1} to ensure consistency between DAEM-derived apparent activation energies to those obtained using the isoconversional method. This optimized protocol was subsequently applied to all natural samples.

We believe that these additions substantially improve transparency of the data analysis workflow.

Additionally, it is unclear how many samples were tested. It is known that the samples came from two locations, but was only one sample from each site tested? Are they representative? After all, the sediment composition will depend on the sampling location, depth, and many other parameters. The sampling methodology needs to be clarified.

We thank the reviewer for raising this important point. We agree that the sediment composition will be various. In total, we tested over 66 samples, including 55 samples from Congo Basin and 11 samples from Lake Cadagno, and repeated measurements. These samples were selected specifically because they represent contrasting organic-rich and sulfur-rich systems suitable for testing the analytical framework, rather than to provide exhaustive spatial characterization of each environment.

The attached PDF file highlights some shortcomings and ambiguities. Furthermore, the conclusions were described very briefly; they should be expanded.

Thank you for your suggestions. We have expanded the Conclusions section (now ~300 words) to summarize the key +methodological advances, main findings from both field sites, and future applications.

"In this study, we present a novel, integrated TGA/DSC-MicroGC analytical system that enables kinetically resolved characterization of geological materials using high-resolution thermal analysis. By combining thermogravimetric analysis, differential scanning calorimetry and ultra-fast gas chromatography within a single experimental framework, this method provides a mechanistic approach for distinguishing complex C- and S-bearing reactive pools based on their thermal reactivity and gas-evolution signature It also quantifies total and fractional redox capacity (*oxidability*) through time-resolved monitoring of oxygen demand during controlled ramped oxidation. These insights about elemental speciation, reaction kinetics, and redox signature cannot be resolved using conventional bulk analyses alone.

Applications to natural archives from the Congo Basin and Lake Cadagno demonstrate the method's broad utility and environmental relevance. In Congo Basin peatland sediments, the method differentiated Thermally labile and refractory organic carbon pools and quantifies their contrasting oxygen demand, providing a new framework for tracing changes in organic matter preservation and paleoenvironmental redox dynamics (Galvez et al., 2026). In Lake Cadagno sediments, our results reveal a diagenetic front defined by a shift in sulfide speciation and apparent activation-energy, providing a direct kinetic proxy for past microbial S cycling and redox evolution. More broadly, the integration of oxygen consumption profiles with evolved gas signatures allows semi-quantitative partitioning of redox-active components among organic matter, sulfur-bearing phases, and Fe-bearing minerals, yielding a kinetic "redox fingerprint" of geological materials.

Overall, this integrated approach moves beyond static compositional measurements toward a mechanistic, high-resolution framework for tracing coupled C-O-S dynamics in Earth materials. The TGA/DSC-MicroGC platform provides a versatile tool for investigating redox conditions, paleoenvironmental change, and biogeochemical reactivity across diverse natural systems. Future applications to marine sediments, soils, and ancient rock archives may further refine our understanding of redox processes across environmental settings and their links to elemental cycling and Earth evolution."

In summary, the article is scientifically sound and clearly structured, but the methodological section could be expanded to provide a more detailed and reproducible description of how kinetic parameters were calculated. Greater clarity in the data analysis workflow and parameter estimation procedure would strengthen the technical rigor of the manuscript.

We thank Reviewer #2 for the constructive comments, which significantly improved the manuscript. In response, we have expanded the methodological description, clarified sample representativeness, strengthened the explanation of parameter estimation and uncertainty treatment, addressed all annotated ambiguities, and revised the Conclusions. We believe these changes have substantially improved the manuscript.

The article requires editorial corrections. For example, in many places, like here, there are missing spaces.

We apologize for these mistakes, and all missing spaces and minor typographical errors have been corrected in the revised version.

how many samples were tested?

In total, we tested 66 samples, including 55 samples from Congo Basin, 11 samples from Lake Cadagno. These samples were selected specifically because they represent contrasting organic-rich and sulfur-rich systems suitable for testing the analytical framework, rather than to provide exhaustive spatial characterization of each environment.

a dash would be better here, not a hyphen, and with spaces at that

Corrected.

the graph in Figure 2 does not indicate such a wide range of distribution

The same, as previous remark

Thank you for your comments. You are right that L-cystine and cellulose decompose primarily within narrower ranges (200–350°C and 250–350°C, respectively). Our original wording (“decomposed between 200°C and 700°C”) was intended to describe the full temperature range until the reaction is complete (including tailing), but we agree that it was misleading given the actual shape of the curves. We have revised the text accordingly.

the abbreviations used require explanation (for example, when first used or in the form of a list at the end of the article)

All abbreviations are now defined on first use.

in this paragraph it is not clear whether the considerations concern oxidation or pyrolysis (compare lines 108 and 109)

We have clarified that all experiments described in Section 3.1 were performed under the oxidative atmosphere (10 mL min^{-1} N_2 + 1 mL min^{-1} O_2)

Which graphs refer to oxidative and non-oxidative conditions? It's not clear.

We agree with the reviewer that the original sentence is confusing. Elemental sulfur undergoes rapid volatilization between 100°C and 300°C under oxidative condition. 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 dO_2 values lower than theoretical predictions. We have revised it accordingly.

as it was mentioned before, the abbreviations need explanation

All abbreviations are now defined on first use.

this is not a sufficient explanation of the content of the figure

Thank you for pointing this out. We have added some explanation for the Figure 3 accordingly.

Where did these activation energy values (160 and 120) come from? Are these average values for some range?

These activation energy values are from a model-free isoconversional method of Vyazovkin (Vyazovkin and Wight, 1999), implemented in the STARe software.

what is shown in Fig. 5 can hardly be called a thermogram

You’re correct. The term “thermograms” in the preceding text refers to the TGA mass-loss curves. We have revised it as “Activation energy distributions” accordingly.

what do the symbols mean: IMB 004 and IMB 090?

IMB 004 and IMB 090 are labeled for two representative sediment samples from the Congo Basin peat core, which was recovered in 2017 from the Ingende Territory (Equateur Province) in the Democratic Republic of Congo.