

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 CaCl_2 addition particularly interesting. The manuscript is well written and organised, and properly referenced. There are some aspects that can be improved significantly:

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.
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?
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.
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.
5. Line 236. What are the mechanisms in which chlorine can influence thermochemical reactions of organic matter?
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.
7. Line 288. Please specify the concentration of HCl or range of concentrations. Using the term "diluted" here is inappropriate.
8. Are the results of Fig S2b post-fumigation and rinsed? Please specify.